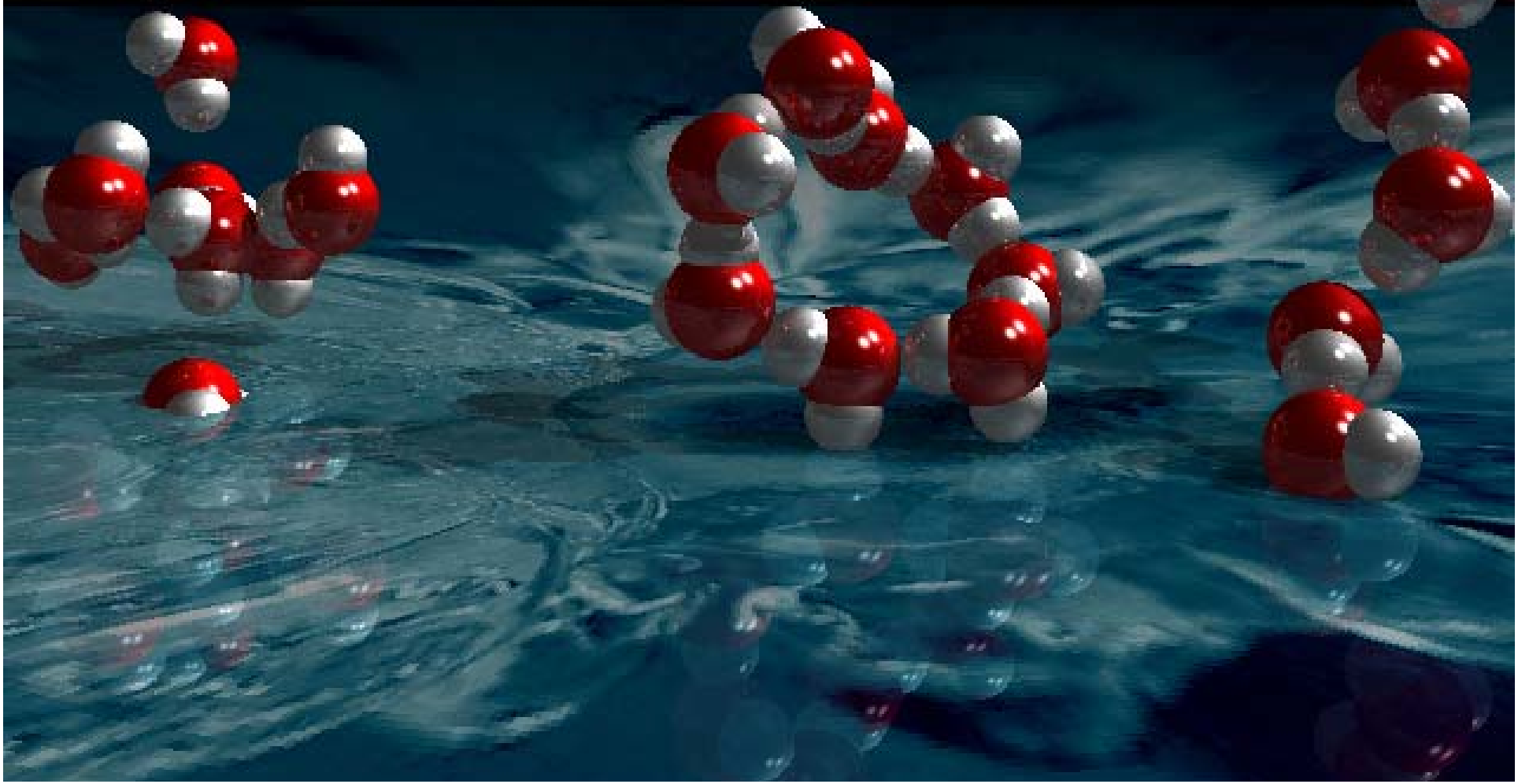
X-ray spectroscopy of Water Controversy

Anders Nilsson, Stanford Synchrotron Radiation Laboratory



Coworkers

Philippe Wernet/Stanford (BESSY)

Uwe Bergman/Stanford

Hirohito Ogasawara/Stanford

Thomas Hirsch/Stanford

Dennis Nordlund/Stanford

Lars Åke Näslund/Stanford

Lars Pettersson/Stockholm

Matteo Cavalleri/Stockholm

Michael Odelius/Stockholm

Clemens Heske/UNLV-Colab

Peter Glatzel/Utrecht

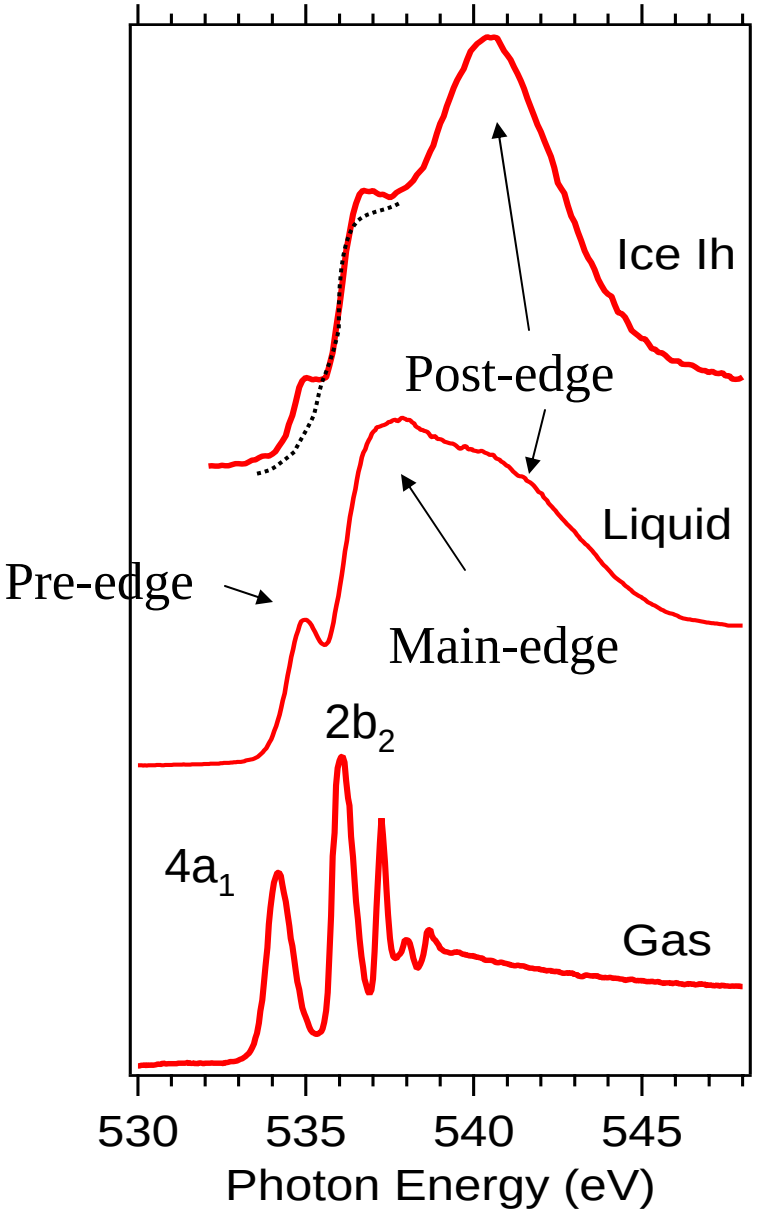
Lars Ojamäe/Linköping

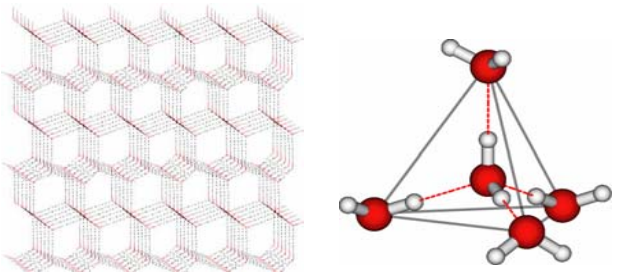
Satish Myneni/Princeton

Henrik Bluhm/ALS

Experiments: APS (BioCat beamline), ALS beamline (8.0, 11.0) and MAXlab (511)

X-ray Absorption Spectroscopy of Water

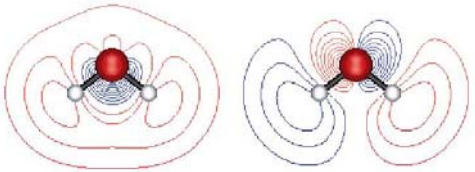




"…making and breaking of H-bonds…"

⇩

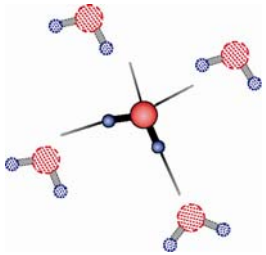
?



$4a_1$ $2b_2$

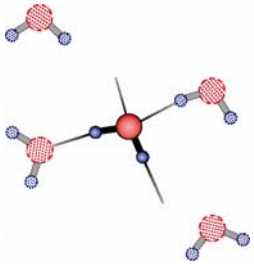
Myneni et.al. *J. Phys. Condens. Matter* **14** (2002) 213

Unequal distortions of H-bonds

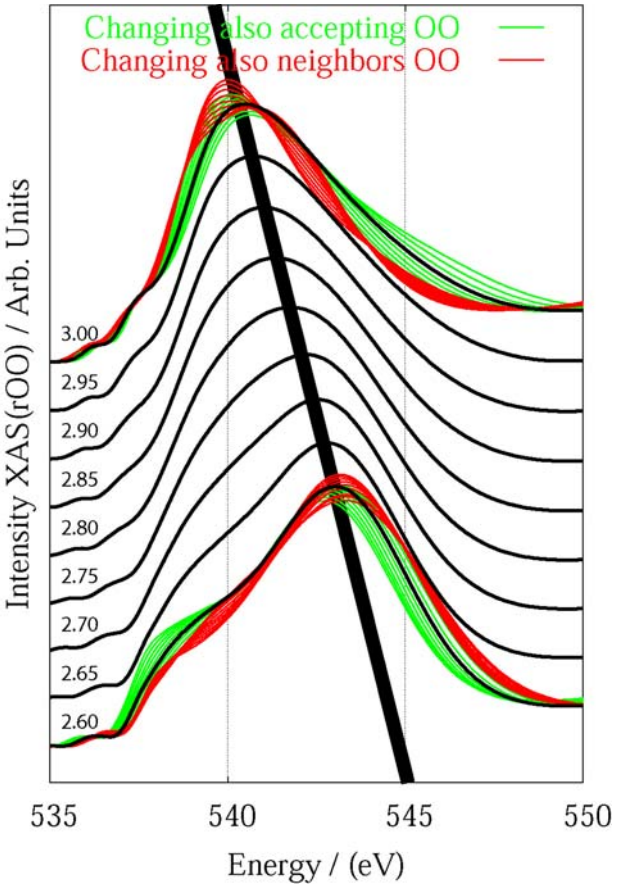


Symmetrical distortions

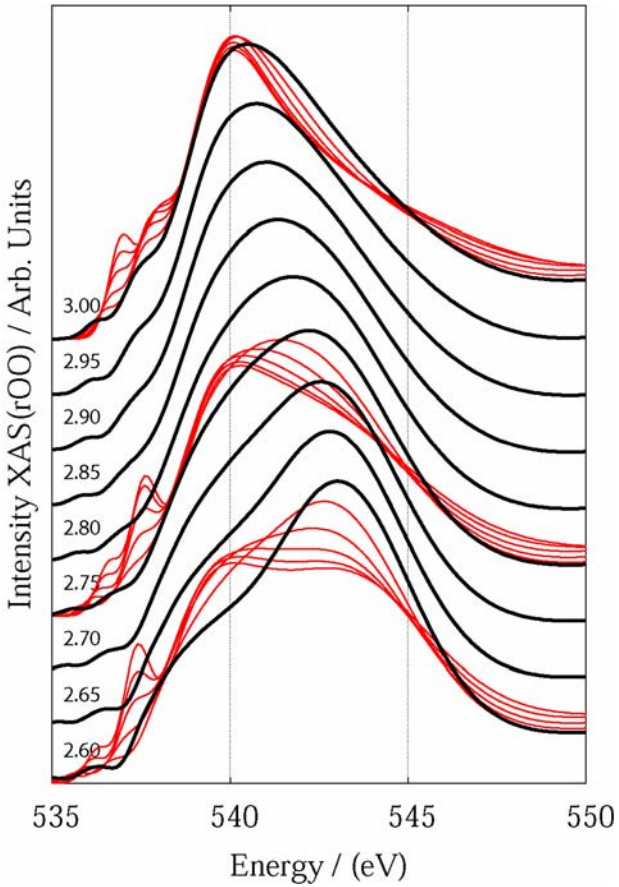
XAS sensitive
to asymmetry
in H-bonding



Asymmetrical distortions

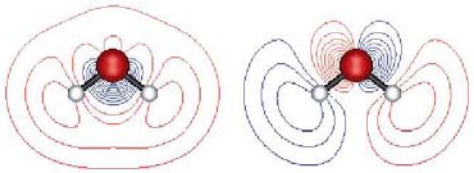


Odelius et. al. unpublished



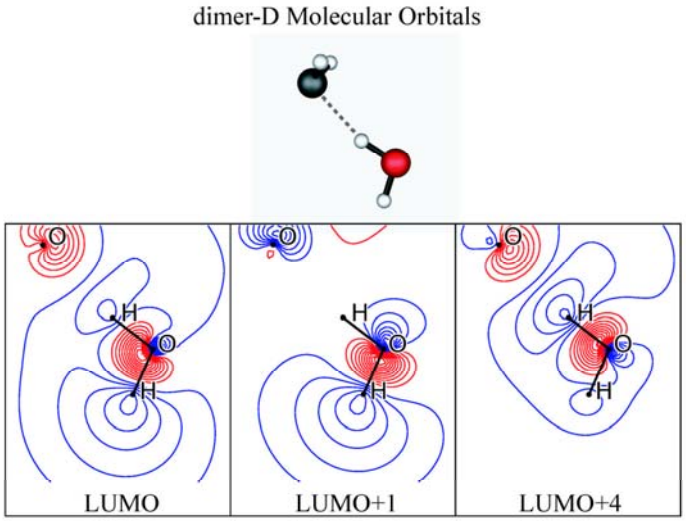
Water Dimer Calculations

Free molecule MO



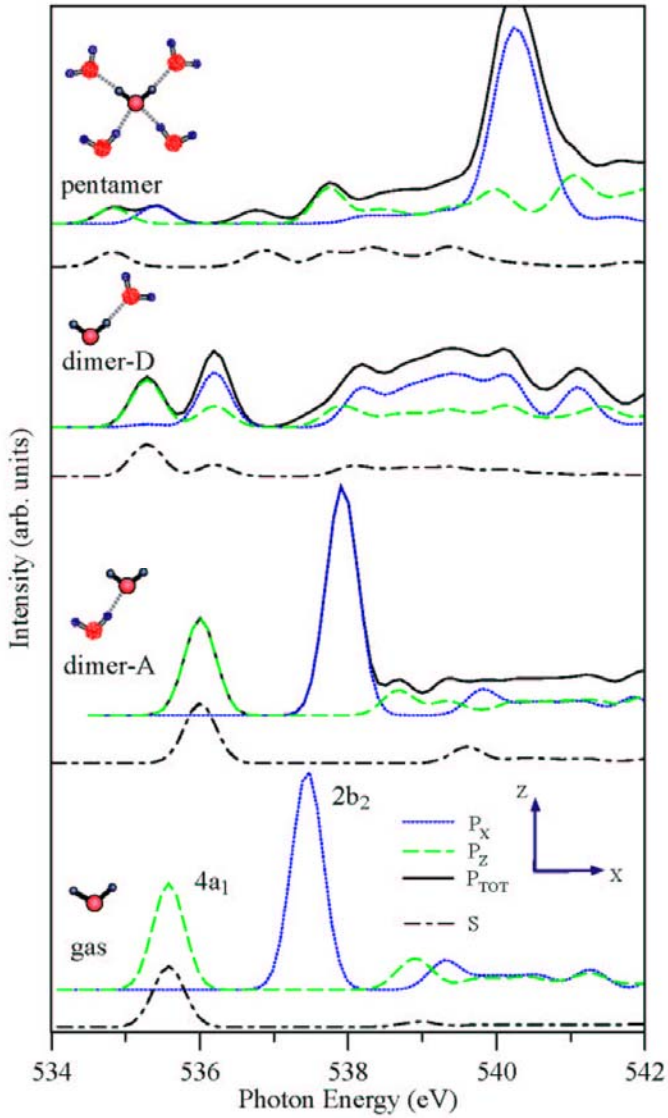
$4a_1$ $2b_2$

Dimer Donor MO



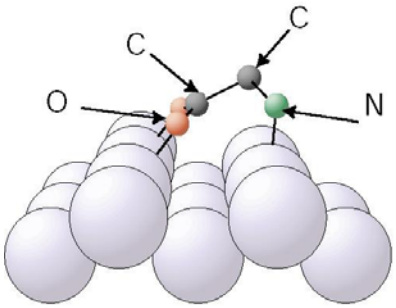
The two OH group different in molecule

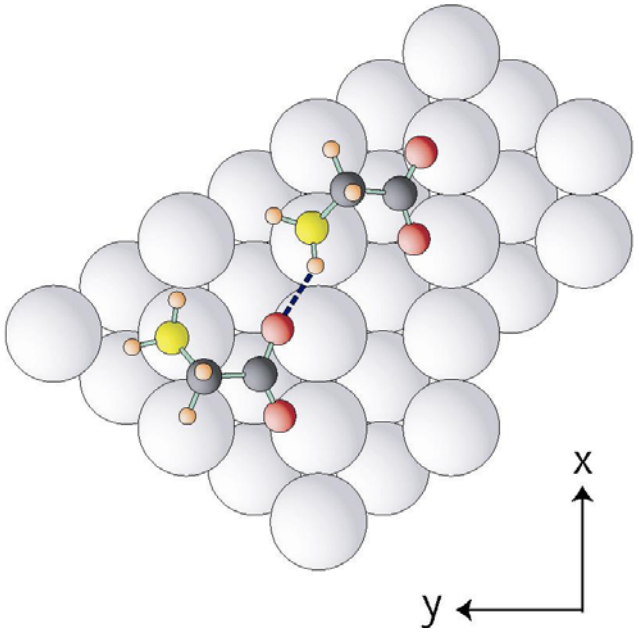
OH group orbital localization

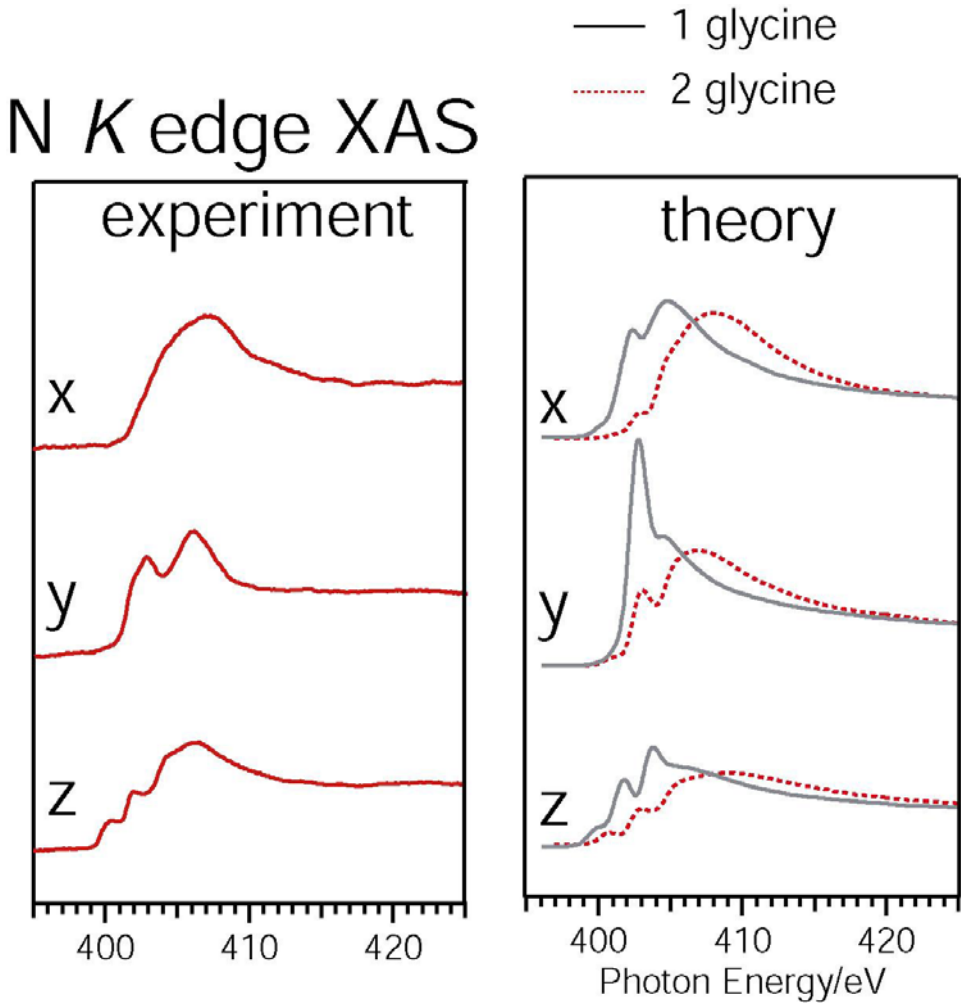


Cavalleri et.al. Chem. Phys. Lett. **364**, 363 (2002)

H-bonding Glycine

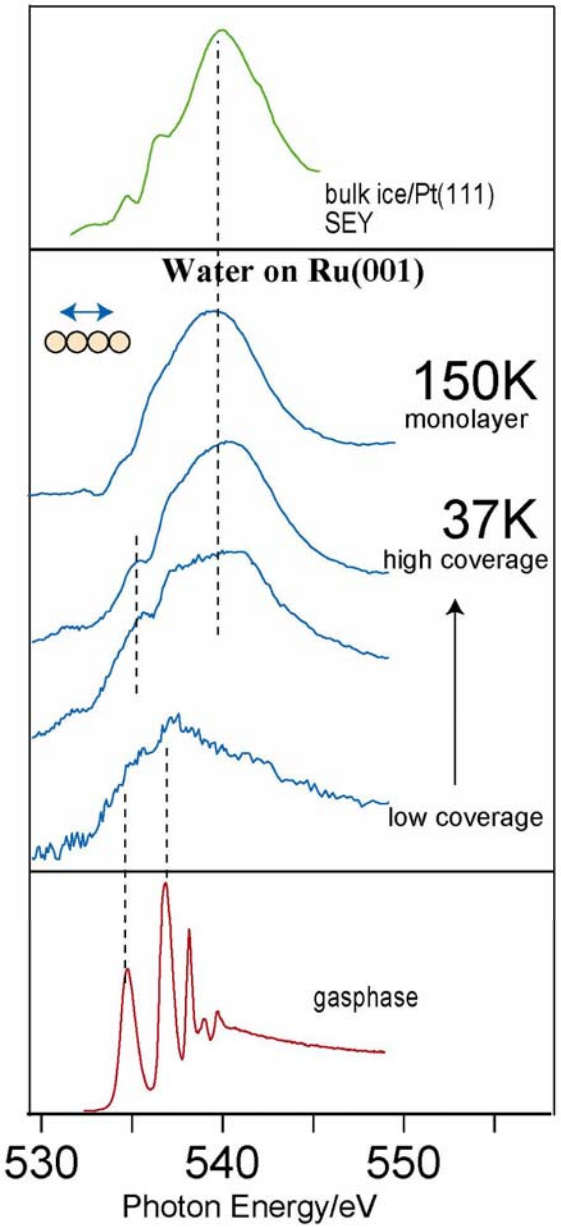


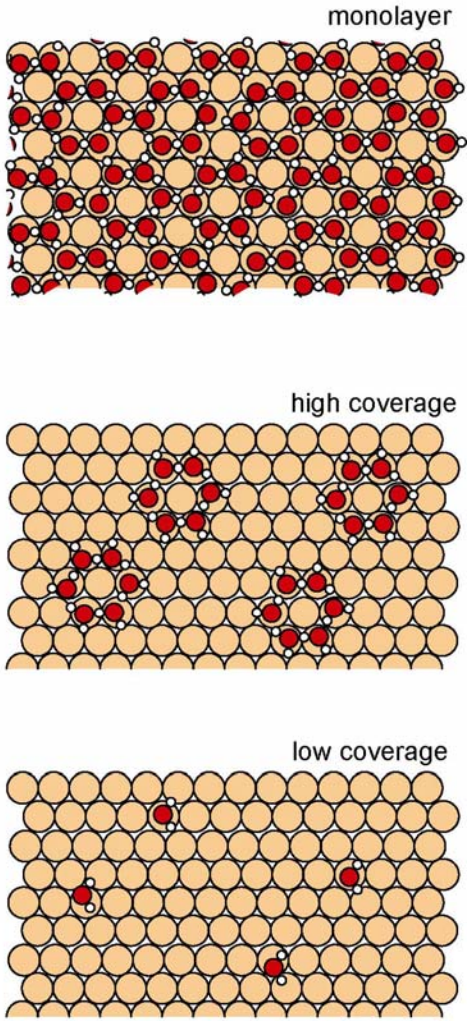


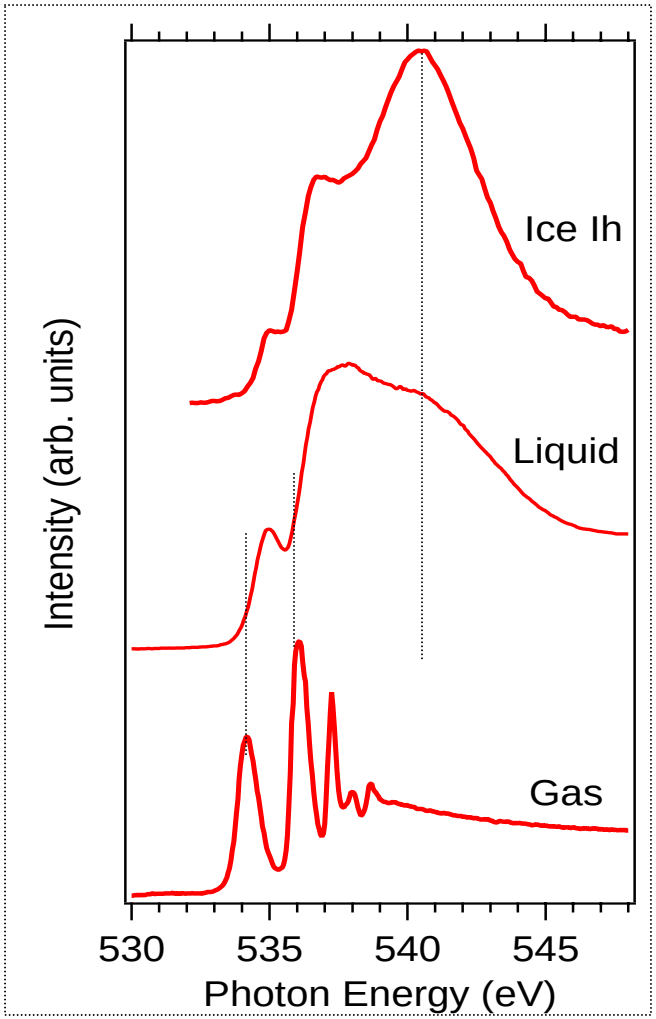


Nyberg et.al *J. Chem. Phys.* **119,** 12577 (2003)

Water clusters on surfaces





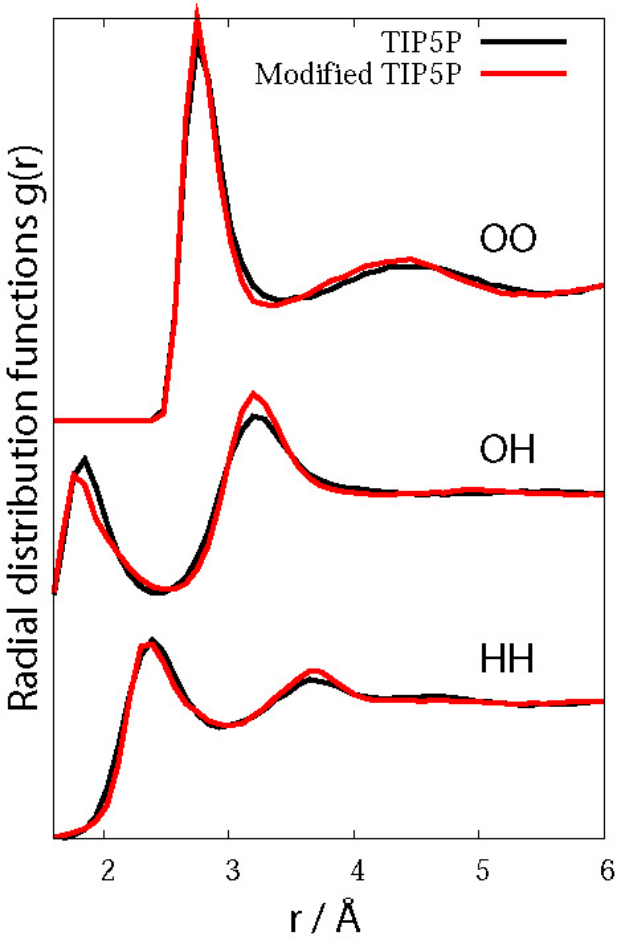


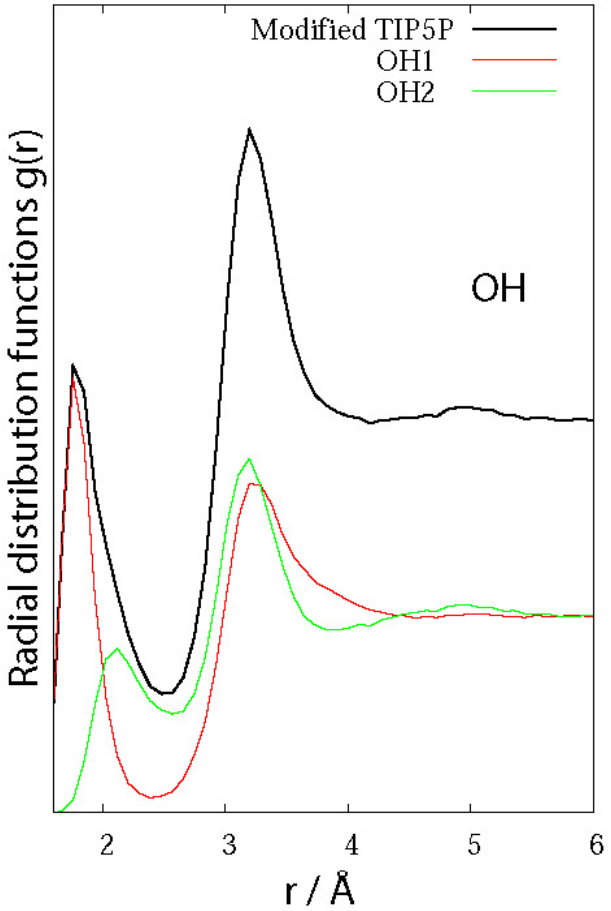
Andersson et. al. unpublished

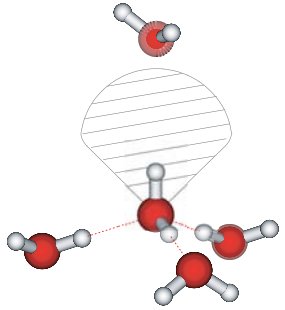
Radial Distribution Functions

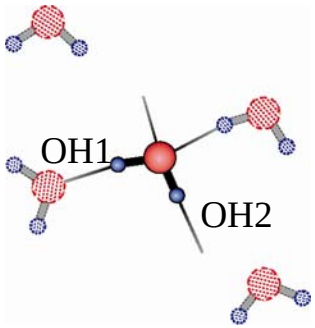
Symmetric distribution TIPP5
(25% SD 75% DD)

Asymmetric distribution TIPP5 modified
(75% SD 25% DD)



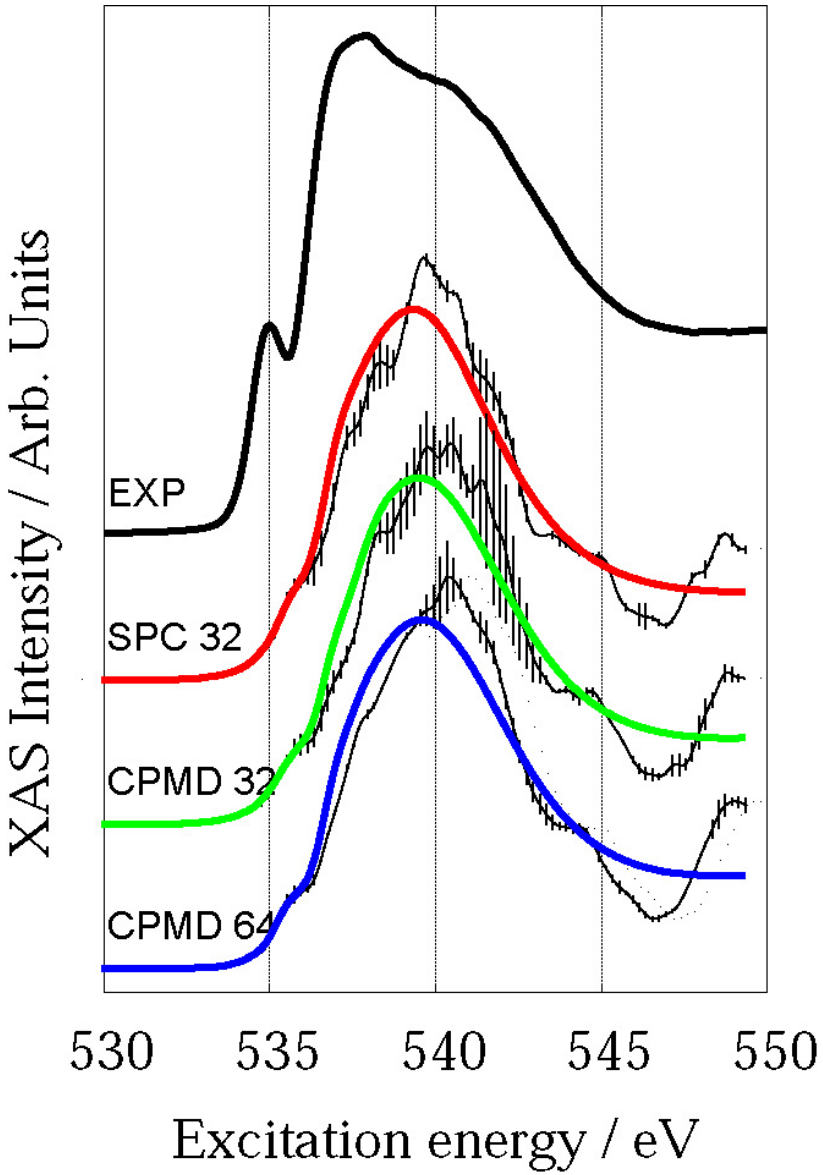






M. Odelius et.al. unpublished

XAS calculated spectra from MD dumps



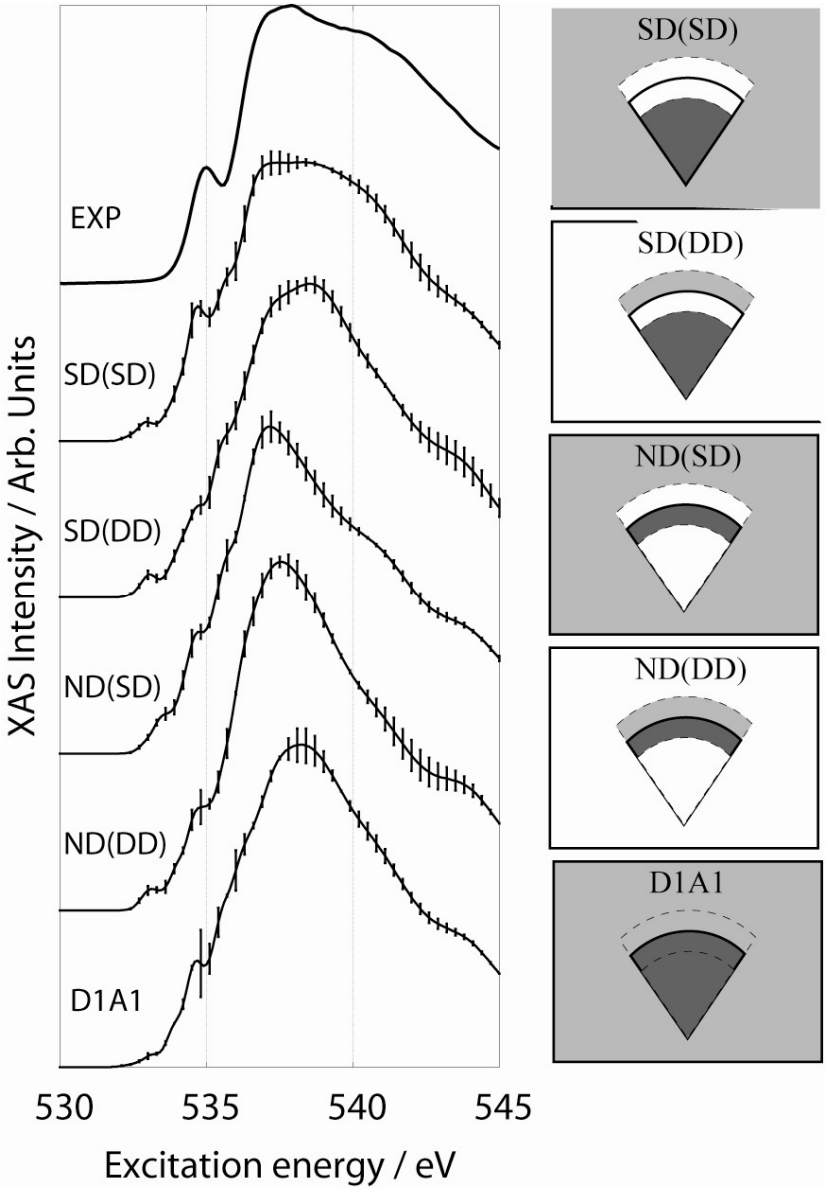
Only post-edge

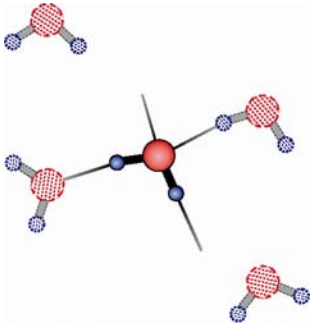
Tetrahedral configurations

Not consistent with experimental spectrum

Odelius et. al. unpublished

Stronger Asymmetry





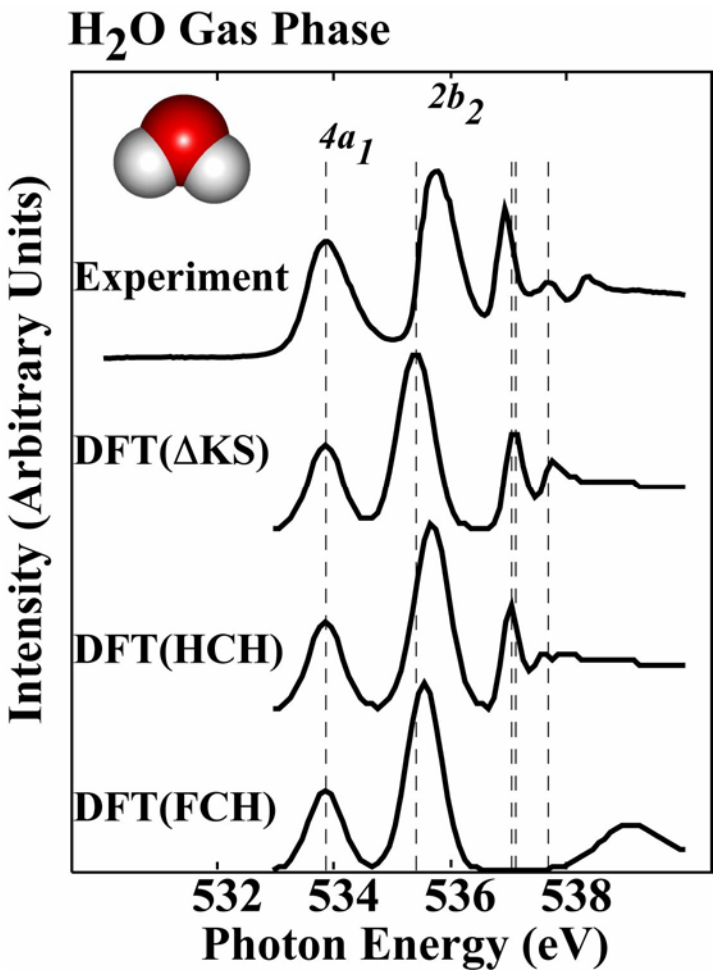
Selecting all SD species from CPMD

Odelius et. al. unpublished

Controversy X-ray Spectroscopy of Water

- Car group,Princeton, MD simulation can explain the XAS spectrum on liquid water using full core hole approximation
- Saykally group, Berkeley, Proposing alternative explanation of XAS based on energy criterium using on Boltzman distribution of temperature dependent population of two different species
- Guo-Nordgren-Ågren-Luo groups, Uppsala, Stockholm, Berkeley, X-ray Emission shows that rings and chains can not exist in the liquid and therefore the tetrahedral model is correct

Approximation for Full Spectrum: Half versus Full Core-Hole Potential



Too much final state screening
Rydberg states pushed up in FCH

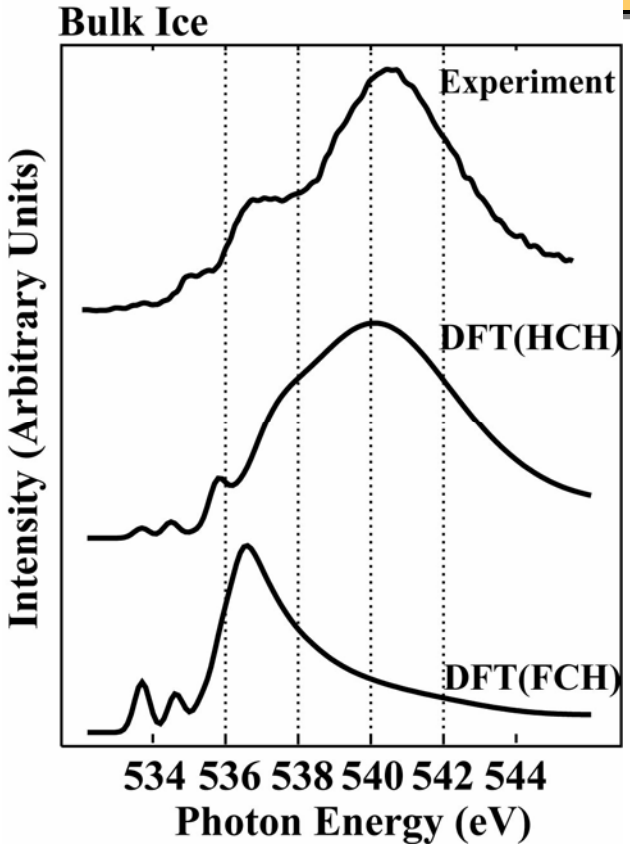
Paper by Hetenyi et al using CPMD claiming agreement for XAS of liquid (19% SD) by using Full Core-Hole potential (J Chem Phys **120**, 8632 (2004))

Final state rule: Energies determined by final state (i.e. H_2F)
Initial state rule: Intensities determined by unoccupied states in ground state

Half Core-Hole or Transition potential (Slater) balances initial and final state effects
Slater transition state $\Delta E \approx \varepsilon_f^{1/2} - \varepsilon_i^{-1/2}$

Cavalleri et al, *Phys.Chem.Chem.Phys* **15** (2005) 2854

Half versus Full Core-Hole Potential



- Intensity localization at on-set of spectrum – excitonic effects with FCH

FCH does not reproduce upwards shift with H-bond formation

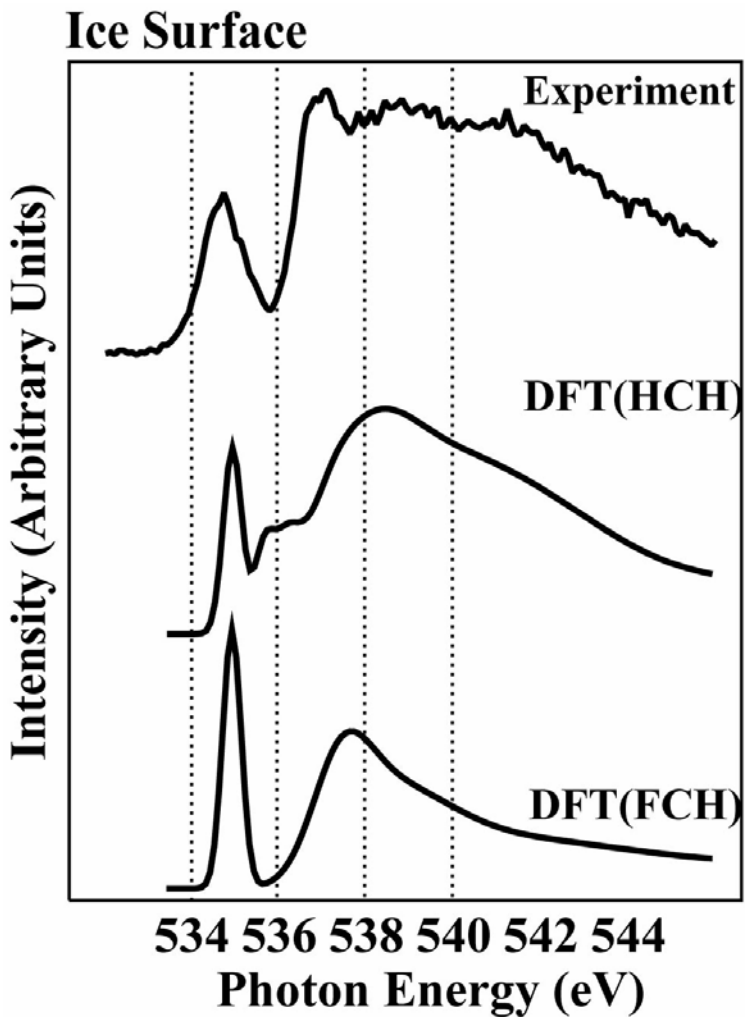
- Contrary to experiment for bulk ice both for shape of spectrum and rate of delocalization (<0.5 fs from RPES)*

- Spectrum positions determined from ΔKS
- calculation (same for FCH and HCH)

- Only intensity shifts

Cavalleri et al, *Phys.Chem.Chem.Phys* **15** (2005) 2854

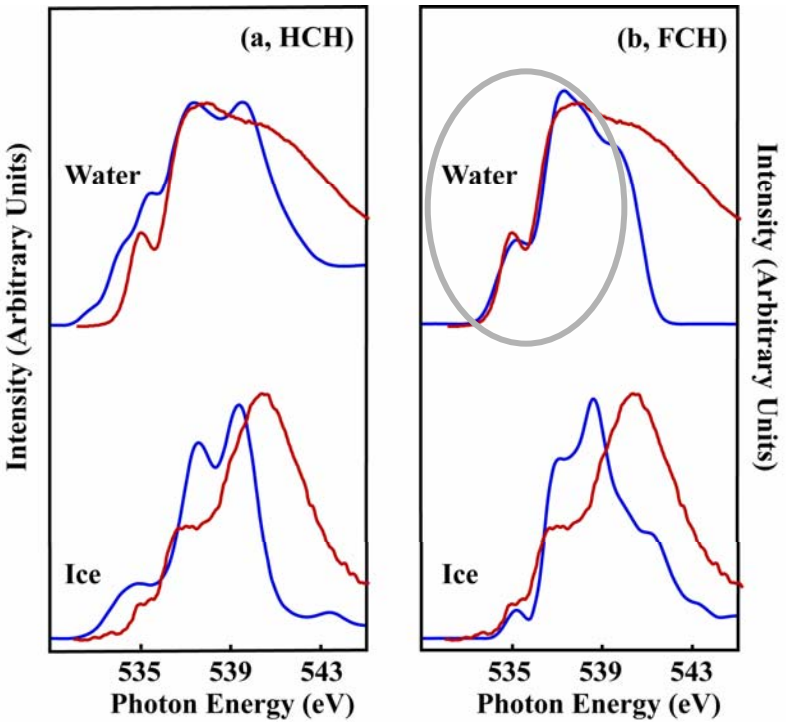
Half versus Full Core-Hole Potential



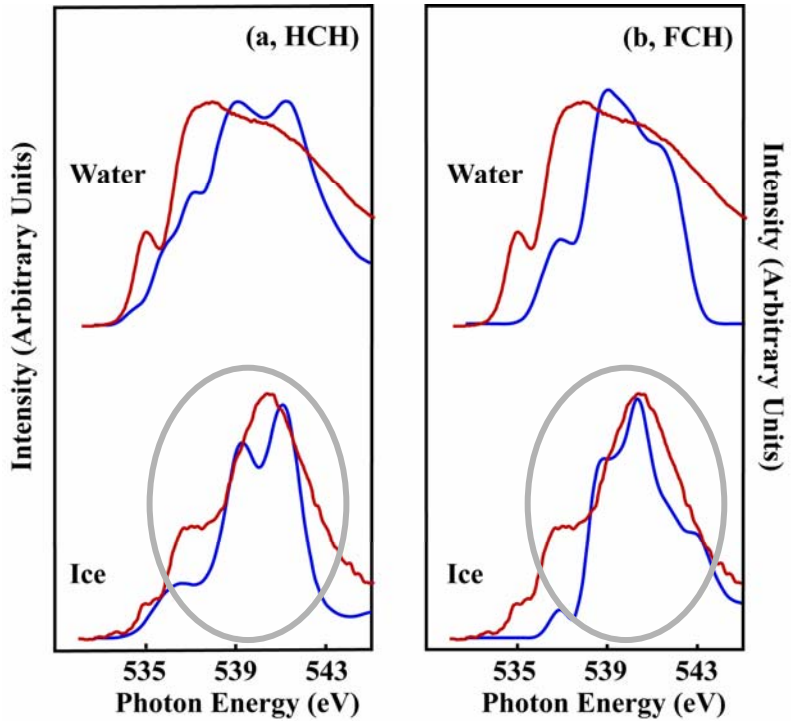
- Ice surface: pre-edge state localized (excitonic)
- RPES shows localization for >20 fs*
- Both HCH and FCH give reasonable spectra
- FCH brings intensity down too much

Cavalleri et al, *Phys.Chem.Chem.Phys* **15** (2005) 2854

Half versus Full Core-Hole Potential: Energy-scale in CPMD



Shift

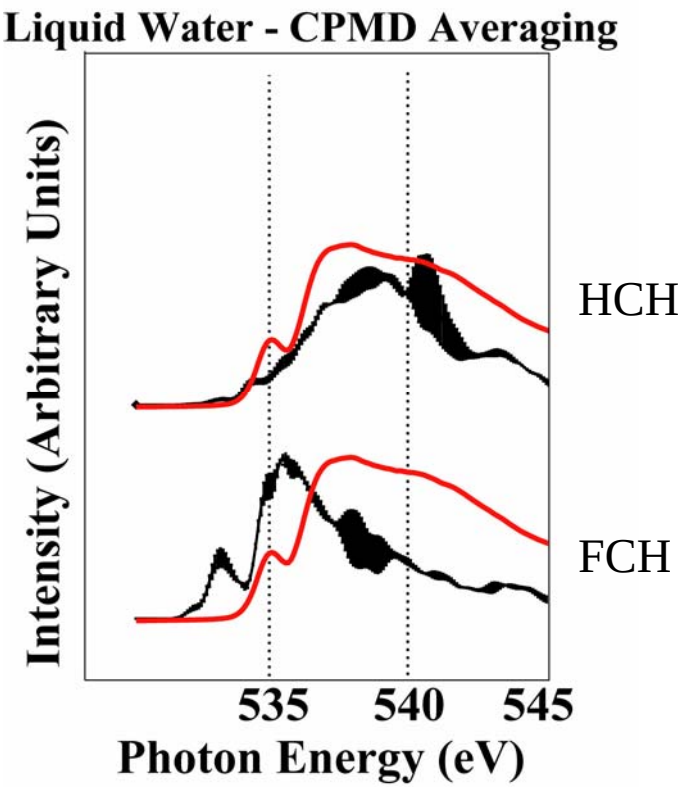


No intrinsic energy scale in pseudo-potential CPMD
In Hetenyi et al spectra have been shifted to maximize agreement for liquid
No agreement for ice Ih

Shift instead to maximize agreement with ice Ih for which the structure IS known...
Corresponds to computed positions
Ice well-represented
Liquid as expected for mainly ice-like coord

Cavalleri et al, submitted

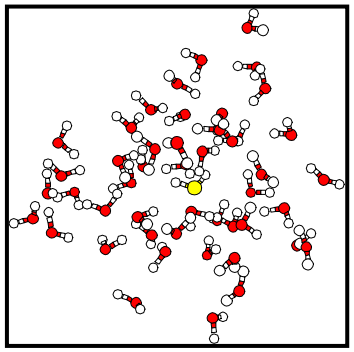
Spectra from CPMD Dump



Same energy positions for HCH and FCH spectra

- Compute spectra for all 32 molecules in representative CPMD dump
- Constant broadening – sum contributions
- 19% SD results in ice-like HCH spectrum
- FCH spectrum not representative
- Both HCH and FCH spectrum positions determined with same ΔKS calculations

Note:
1) Spectroscopy ultrafast
   → atoms frozen
2) 1s hole localized
   → no strong correlation
   (*cf* optical excitations)



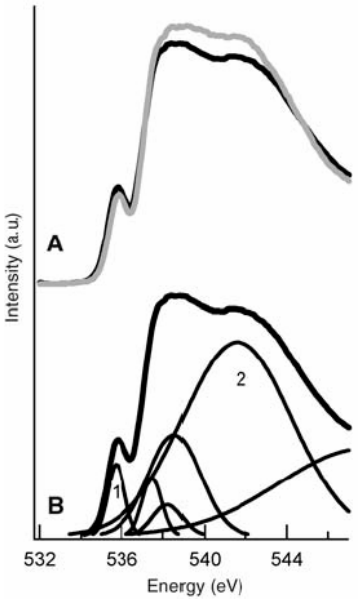
Energetics of Hydrogen Bond Network Rearrangements in Liquid Water

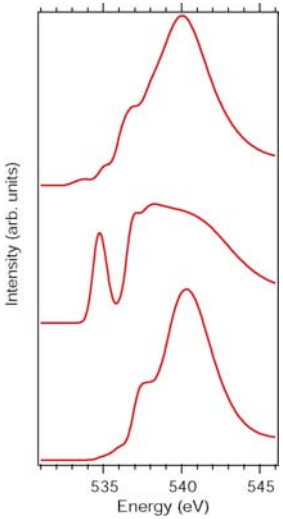
Jared D. Smith, Christopher D. Cappa, Kevin R. Wilson, Benjamin M. Messer, Ronald C. Cohen, Richard J. Saykally*

A strong temperature dependence of oxygen K-edge x-ray absorption fine structure features was observed for supercooled and normal liquid water droplets prepared from the breakup of a liquid microjet. Analysis of the data over the temperature range 251 to 288 kelvin (–22° to +15°C) yields a value of 1.5 ± 0.5 kilocalories per mole for the average thermal energy required to effect an observable rearrangement between the fully coordinated ("ice-like") and distorted ("broken-donor") local hydrogen-bonding configurations responsible for the pre-edge and post-edge features, respectively. This energy equals the latent heat of melting of ice with hexagonal symmetry (ice Ih) and is consistent with the distribution of hydrogen bond strengths obtained for the "overstructured" ST2 model of water.

Science **306** (2004) 852

Temperature dependence





Saykally et al have measured TEY XAS on liquid microjet at different temperatures

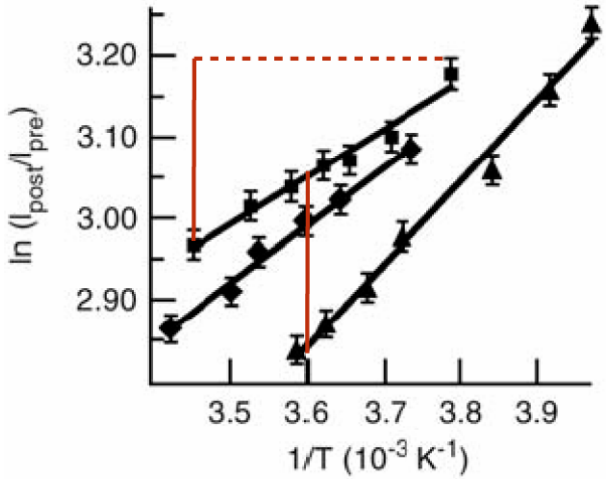
They do XPS-like analysis assuming pre-edge is SD species and post-edge DD

$$\ln\left(\frac{I_{post}}{I_{pre}}\right) = \ln\left(\frac{\sigma_{DD}}{\sigma_{pre}}\exp(\Delta E / RT)\right) =$$

$$\ln\left(\frac{\sigma_{DD}}{\sigma_{pre}}\right) + \Delta E / RT$$

They claim 1.5±0.5 kcal/mol for ΔE

However, SD species contribute to post-edge and the analysis is more involved...



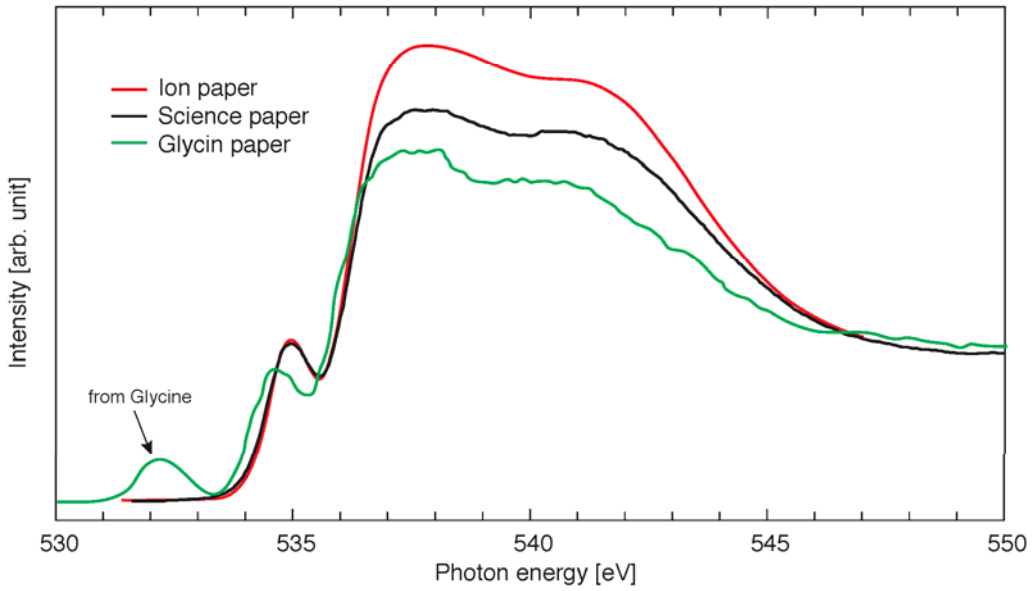
The ratio for a specific temperature, but measured on different occasions varies more than the total variation of one of the slopes!

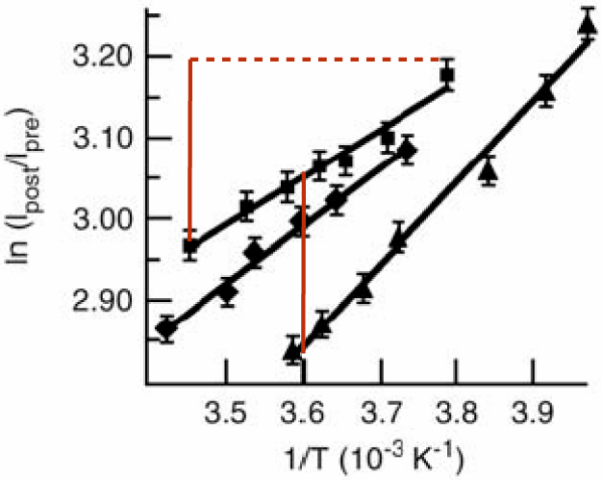
Slope varies 1.2-1.8 kcal
Absolute intensities 21%

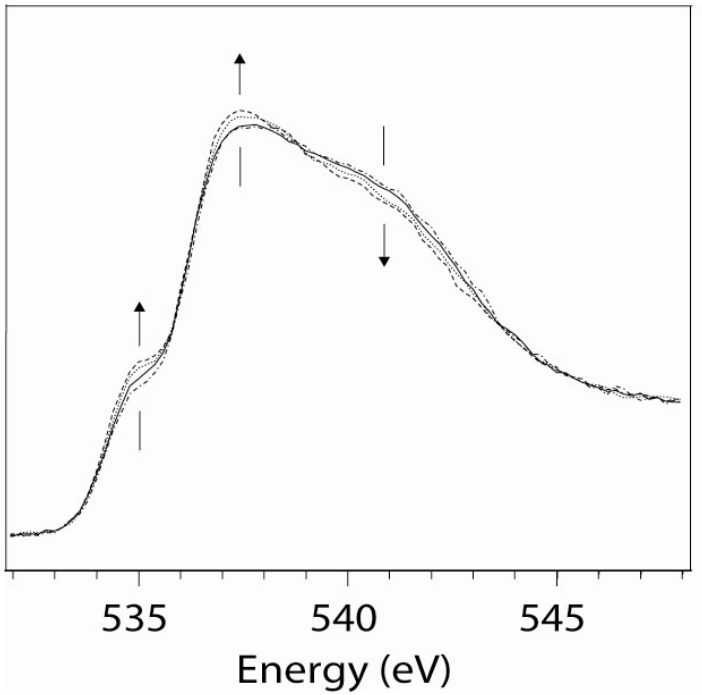
Spectra Quality

Publicated water spectra from Saykally's group

Ion paper - J.Phys. Chem. B 109, 7046.
Science paper - Science 306, 851.
Glycine paper - J.Phys. Chem. B 109, 5375.



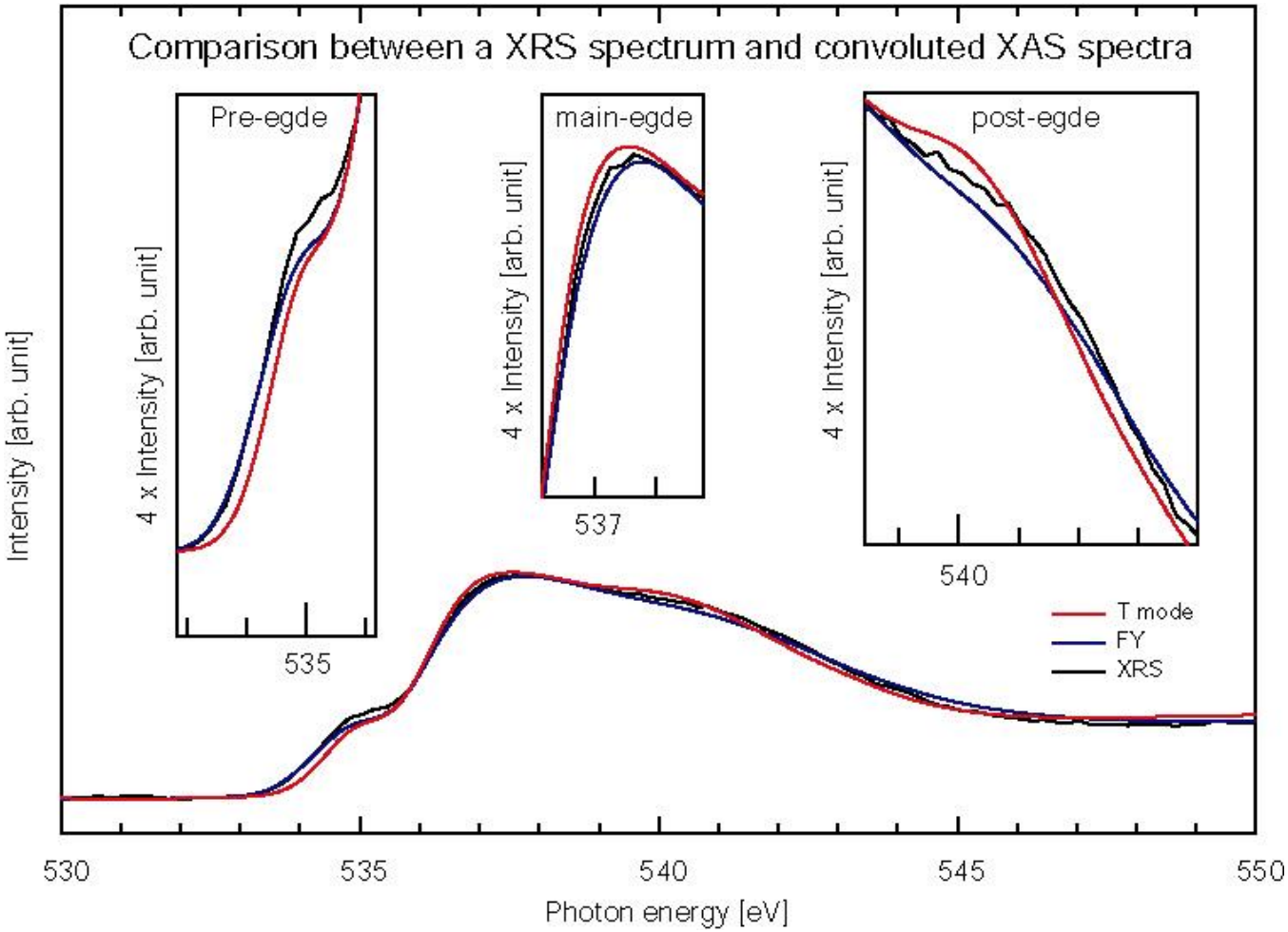




Temperature dependent X-ray Raman
4-90 C

Different measurements methods

Bulk sensitive XAS



Transmission

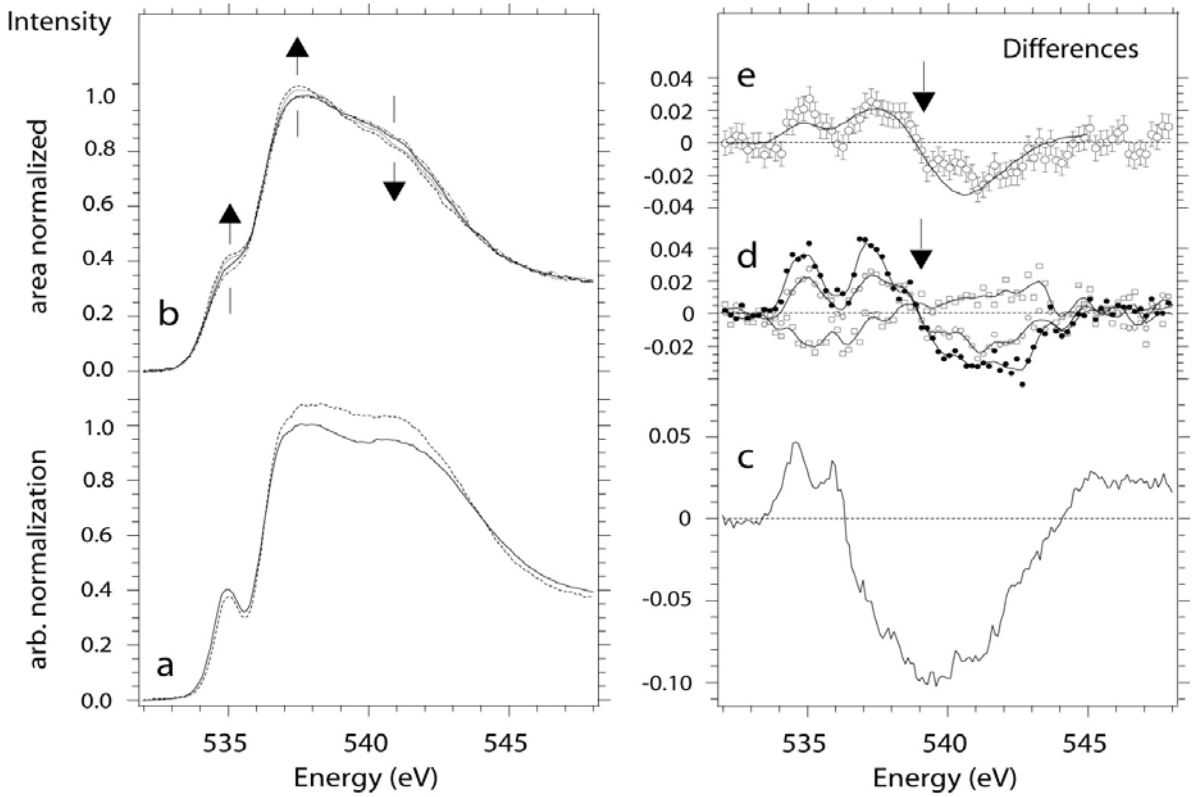
Fluorescence

X-ray Raman

Temperature dependence

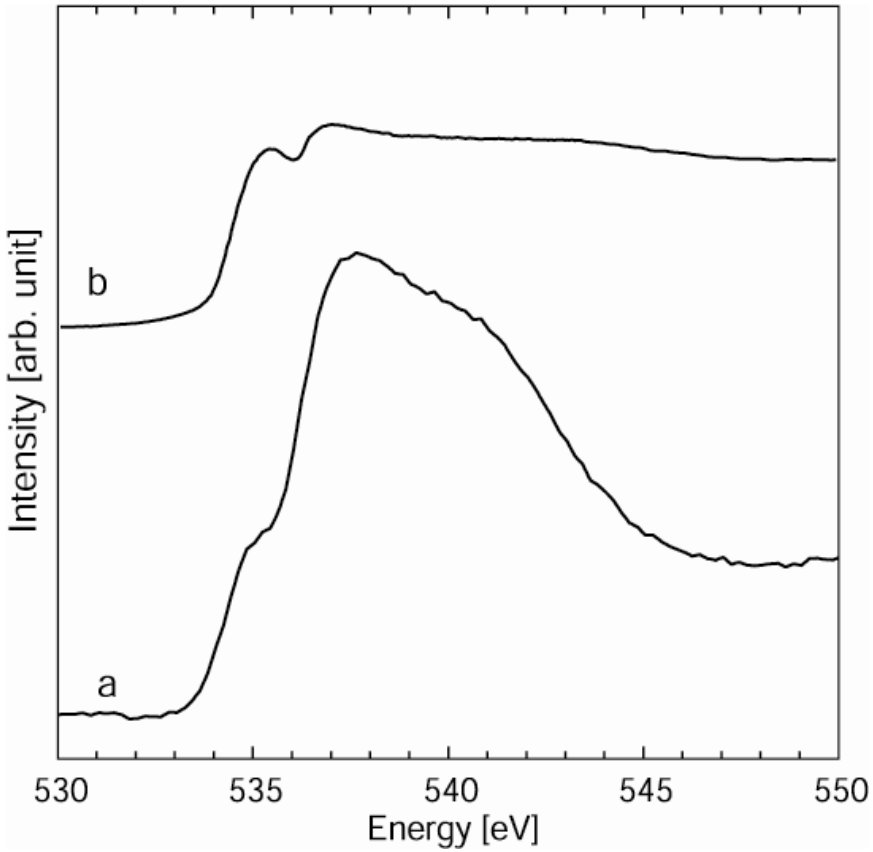
X-ray Raman

Smith el al



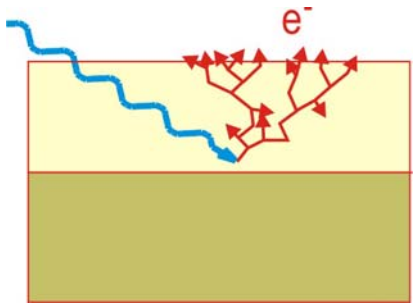
Nilsson et.al. *Science* **308** (2005) 793a

Saturation effects in electron yield



Electron yield in He gas

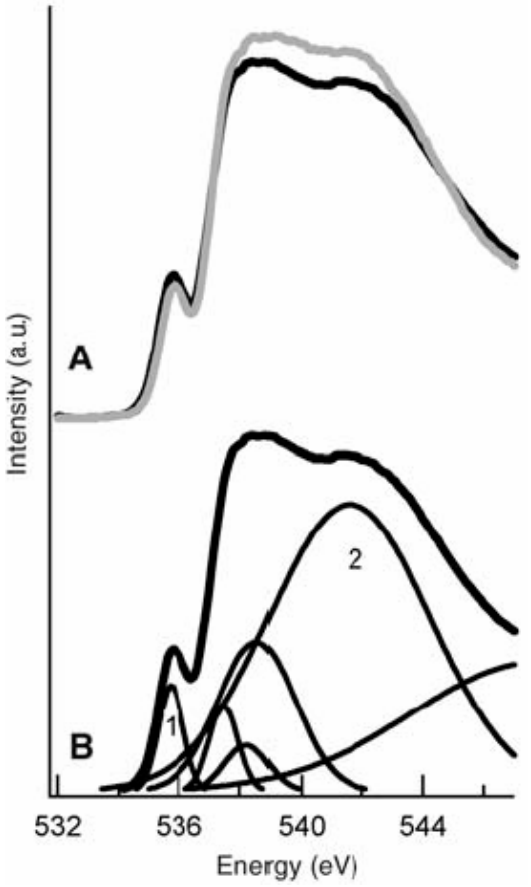
X-ray Raman spectroscopy

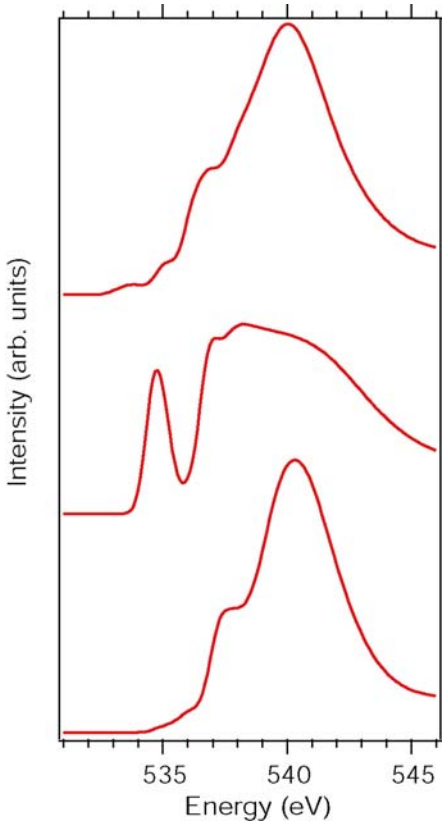


Spectral analysis

Presence of both DD and SD species at post-edge modifies slope:

$$\Delta E = \Delta E'(1+\frac{0.5 * N_{SD}[T_0]}{N_{DD}[T_0]}\exp(\frac{\Delta E}{R}(\frac{1}{T_0}-\frac{1}{T_1}))) \quad > \Delta E'$$





XRS inherently free from saturation Dipole limit within 1-2%

Using the experimentally determined distributions at 100 K (ice) and 25 °C we instead obtain ΔE = 1-4 kcal/mol

Energy Criterium

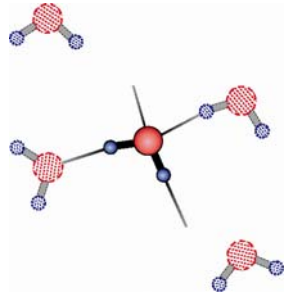
Heat of melting of ice is around 12 % of the sublimation energy of ice

3.5 HB ?

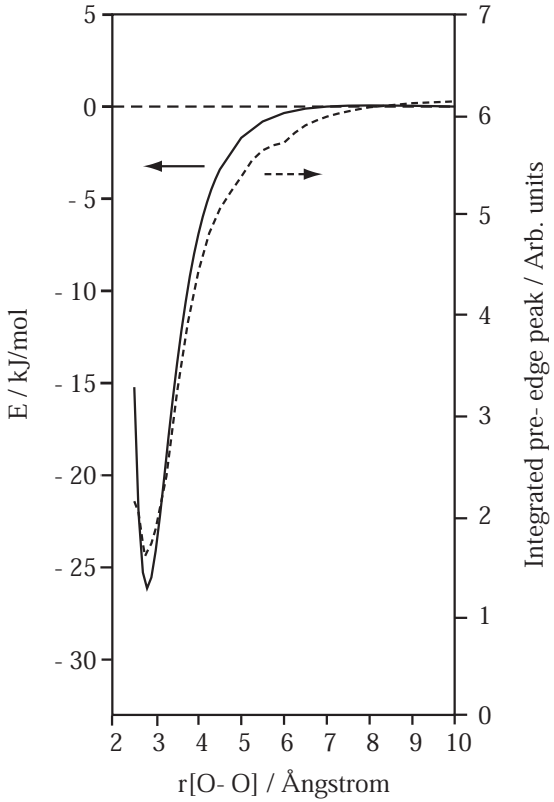
Broken bond is a weak H-bond 40 % lost at cone boundary

Energy per bond kcal/mole

2HB	6.85
3HB	5.29
4HB	6.33



Energy to break an H-bond



At ambient conditions we have 80% SD (2HB) and 20% DD (4HB)

14.7% energy of melting/sublimation

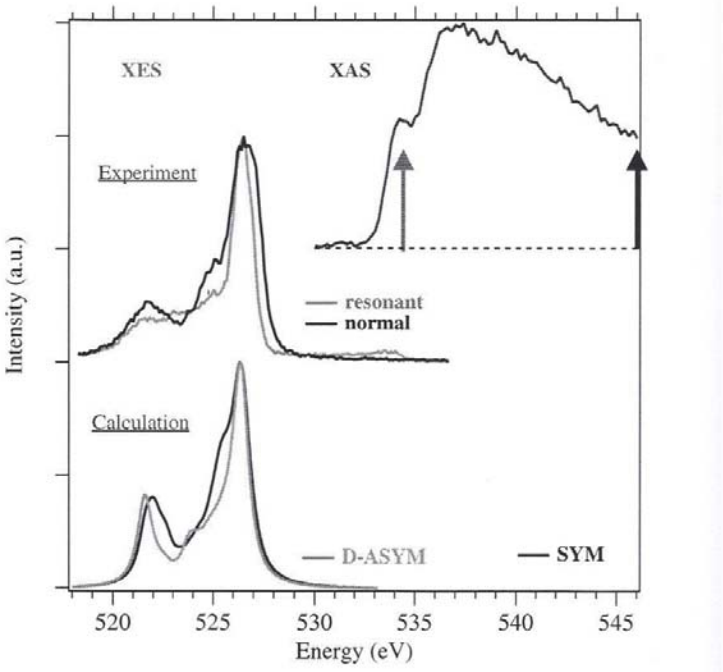
Bending instead of elongation?

Assuming 50% SD with all in 3HB

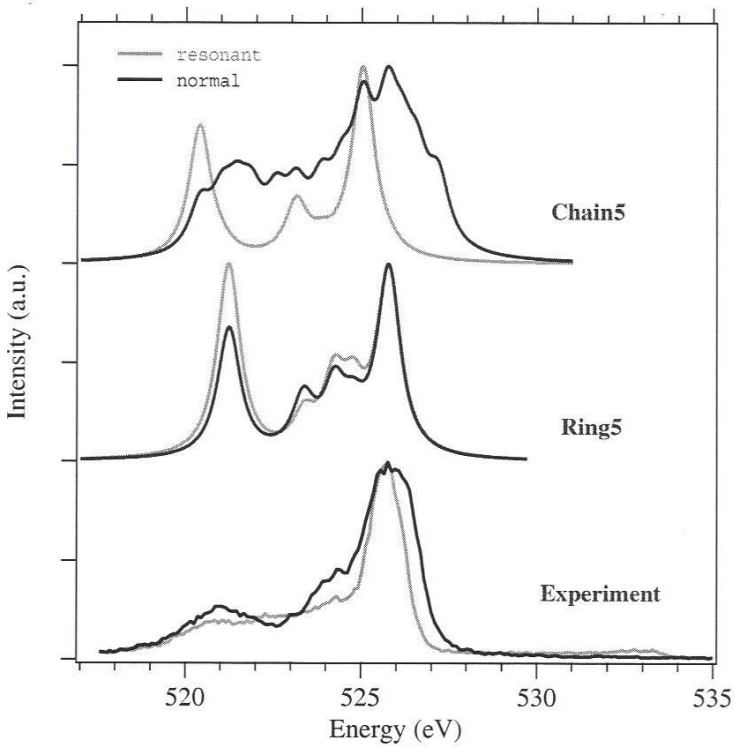
15 % energy of melting/sublimation

XES of Liquid Water

X-ray Emission Spectroscopy



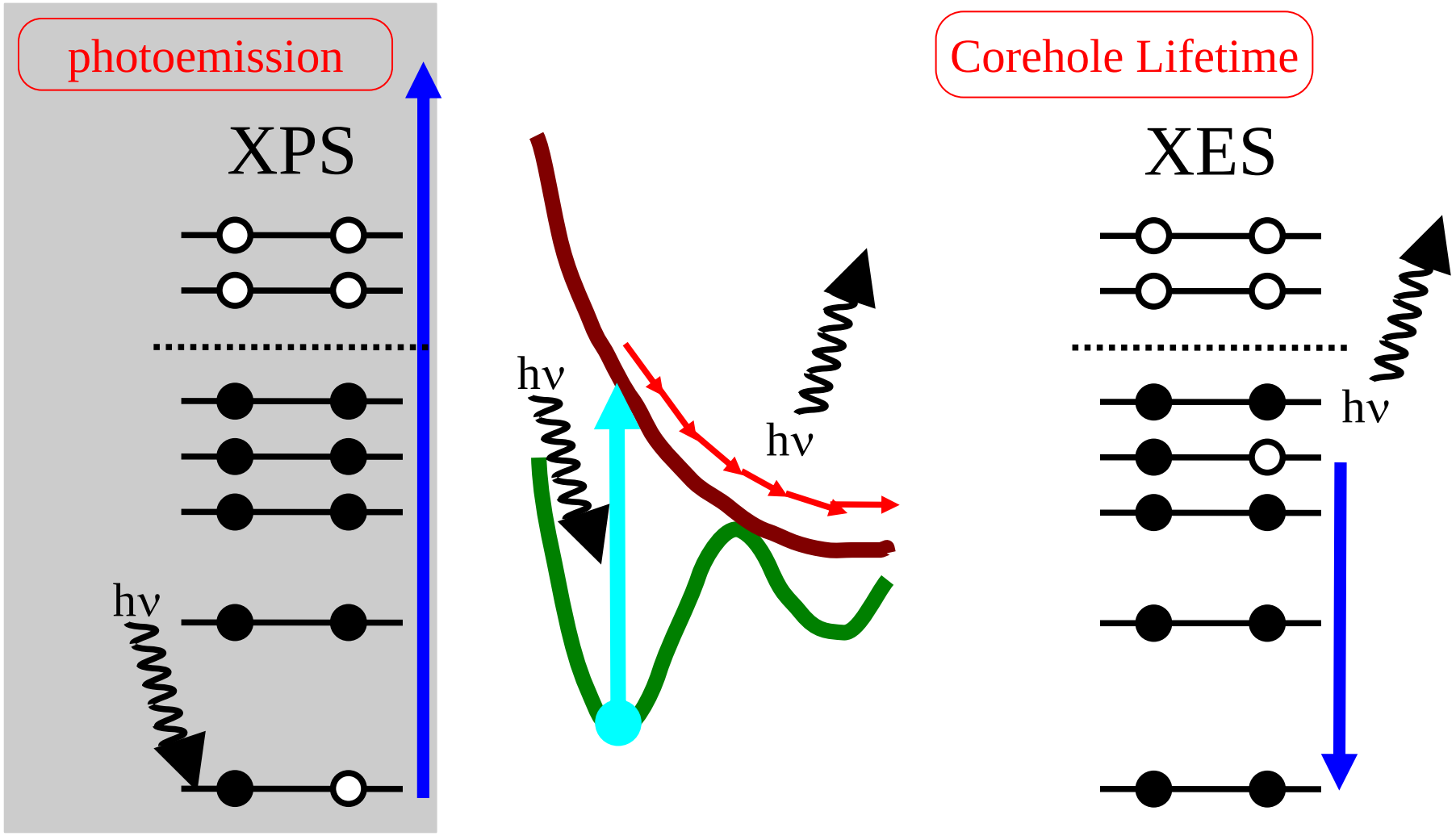
Theory small clusters with
a dielectric continuum



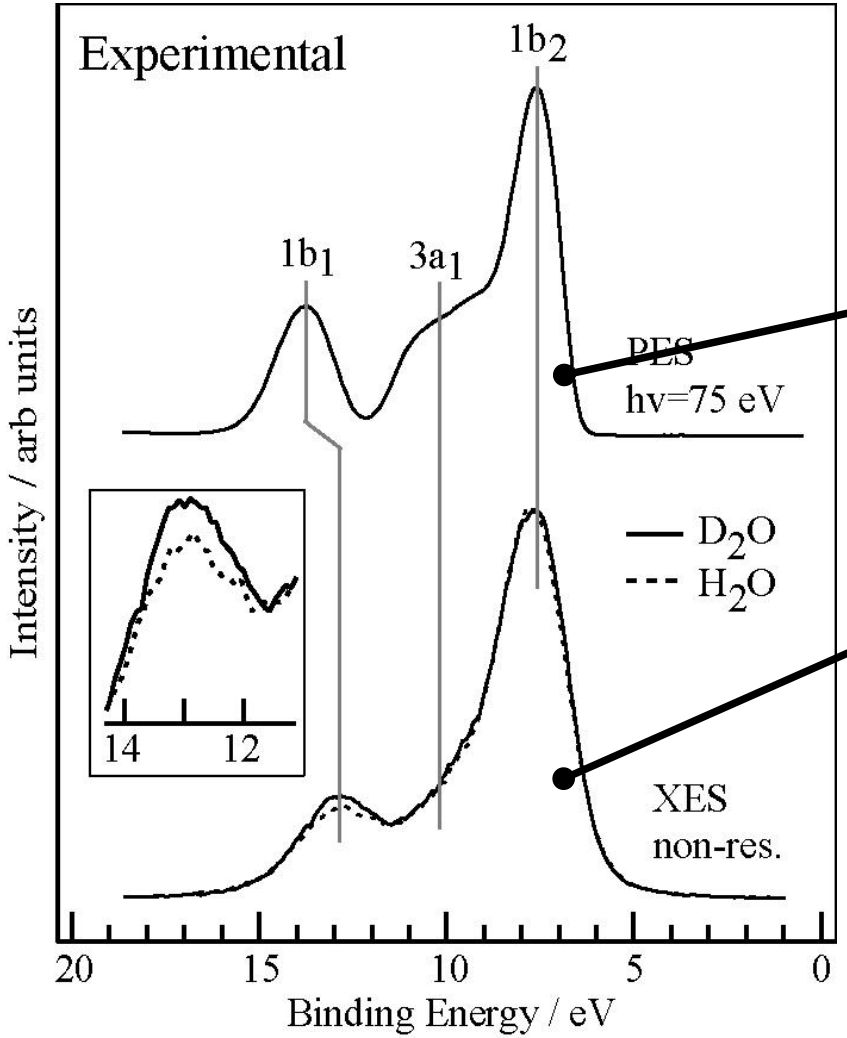
Kashtanov PhD thesis , KTH (Stockholm) 2005

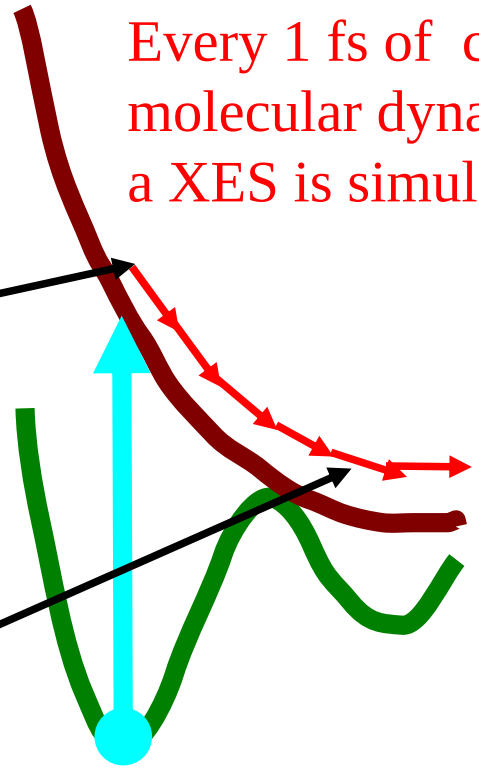
Guo et.al. *Phys. Rev. Lett.* **89**, 137402 (2002).

Nuclei dynamics



The X-ray Emission Spectrum of Ice

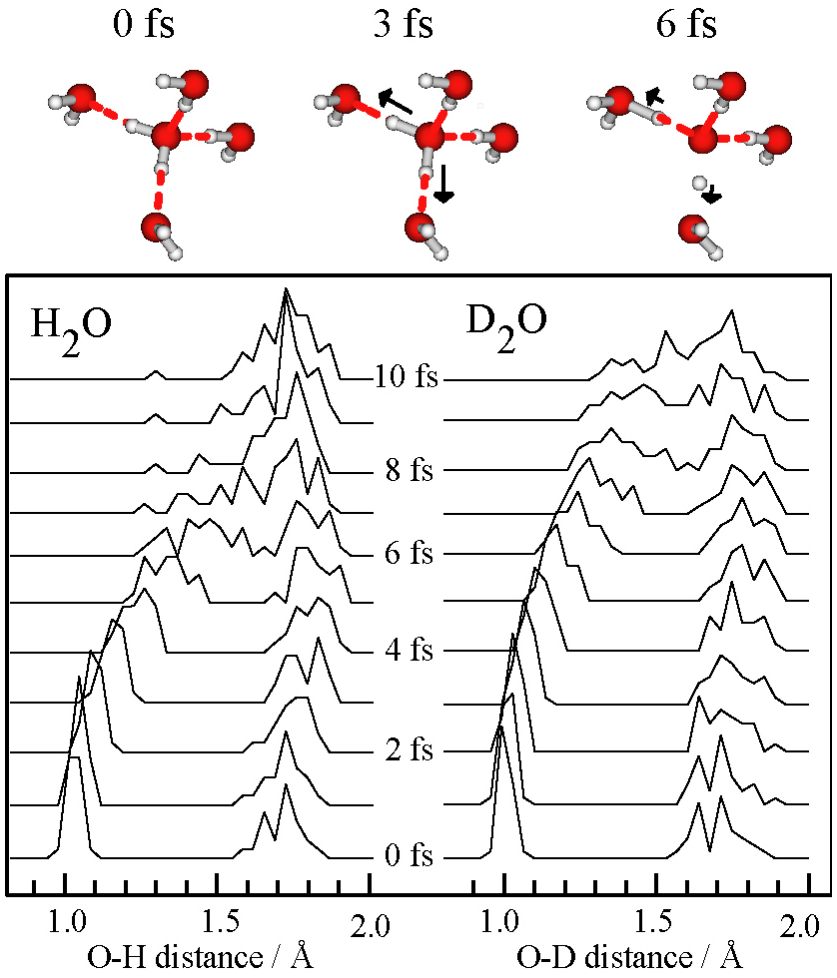


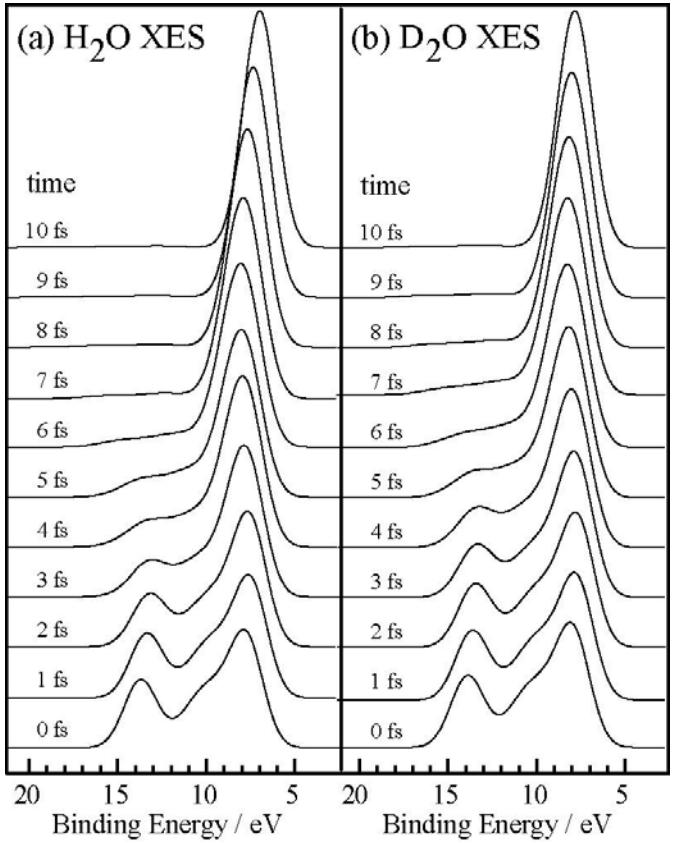


Every 1 fs of core-excited-state molecular dynamics simulation, a XES is simulated

B.Brena et al. PRL **93**,148302 (2004)

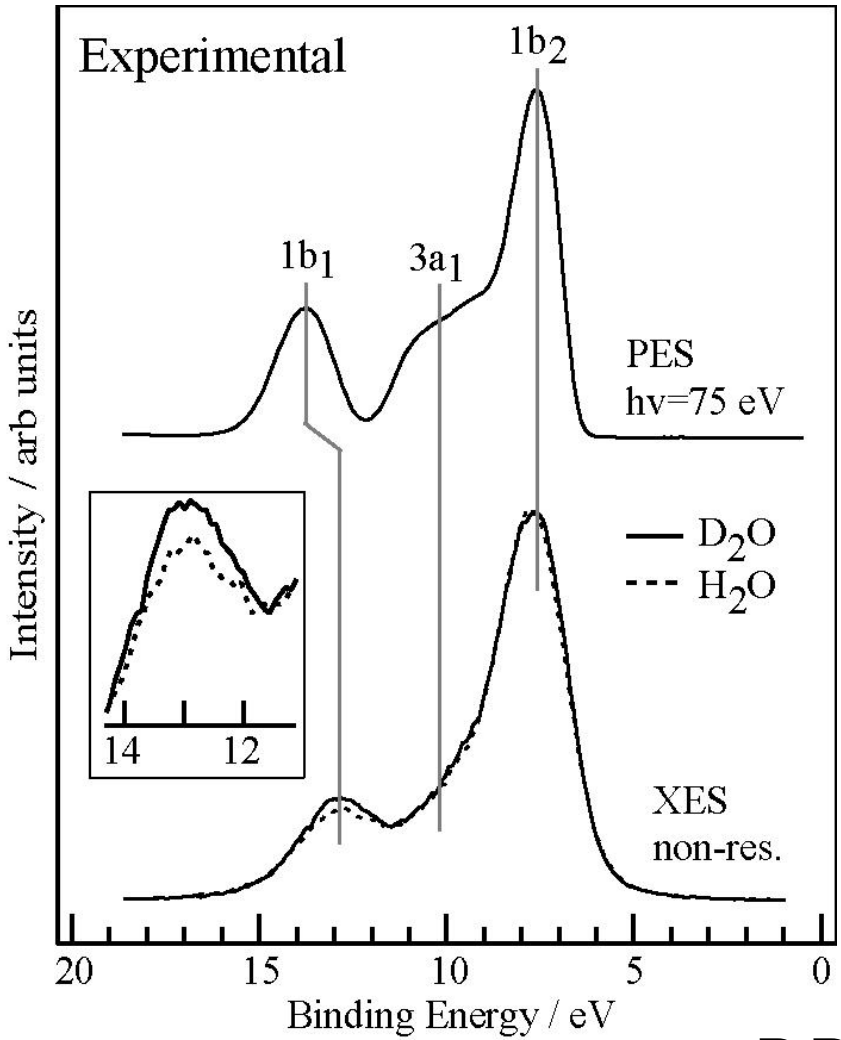
Water dissociation

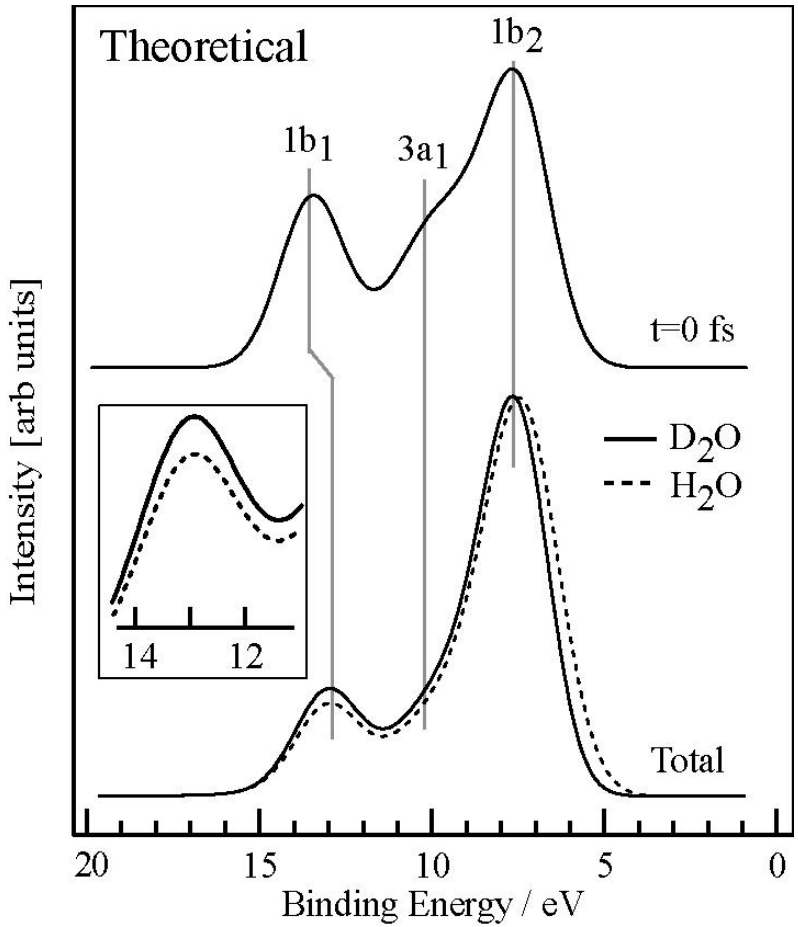




B.Brena et al. PRL **93**,148302 (2004)

Comparison Experiment and Theory

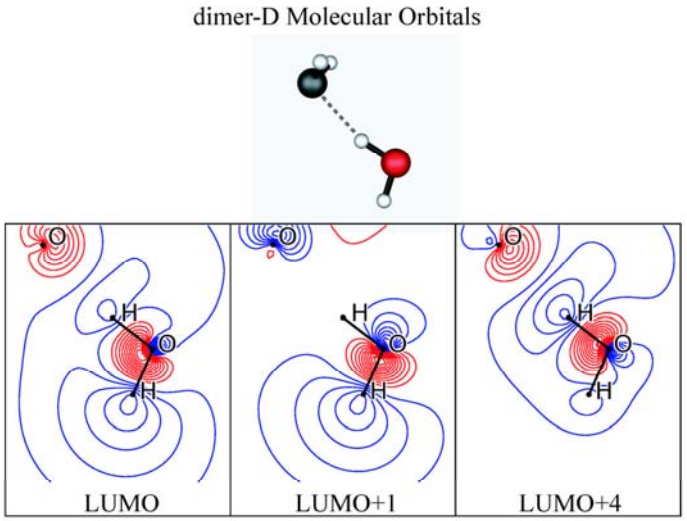


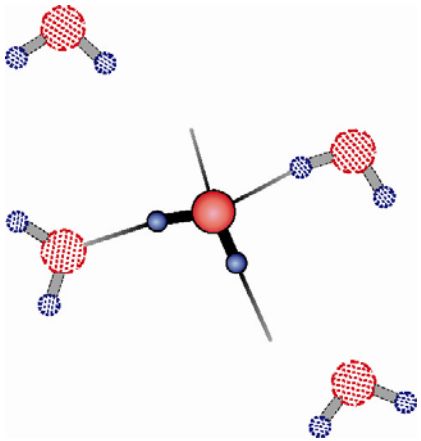


B.Brena et al. PRL **93**,148302 (2004)

Liquid Water

Clemens Heske presentation

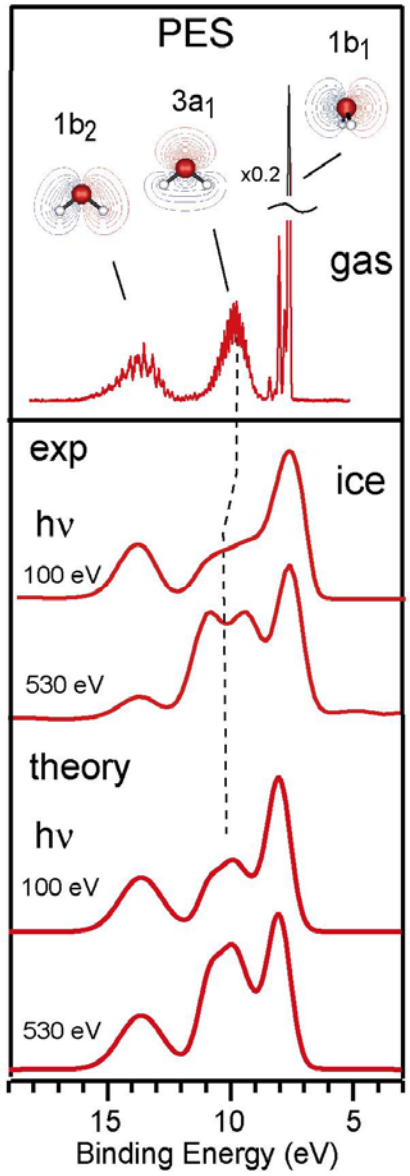


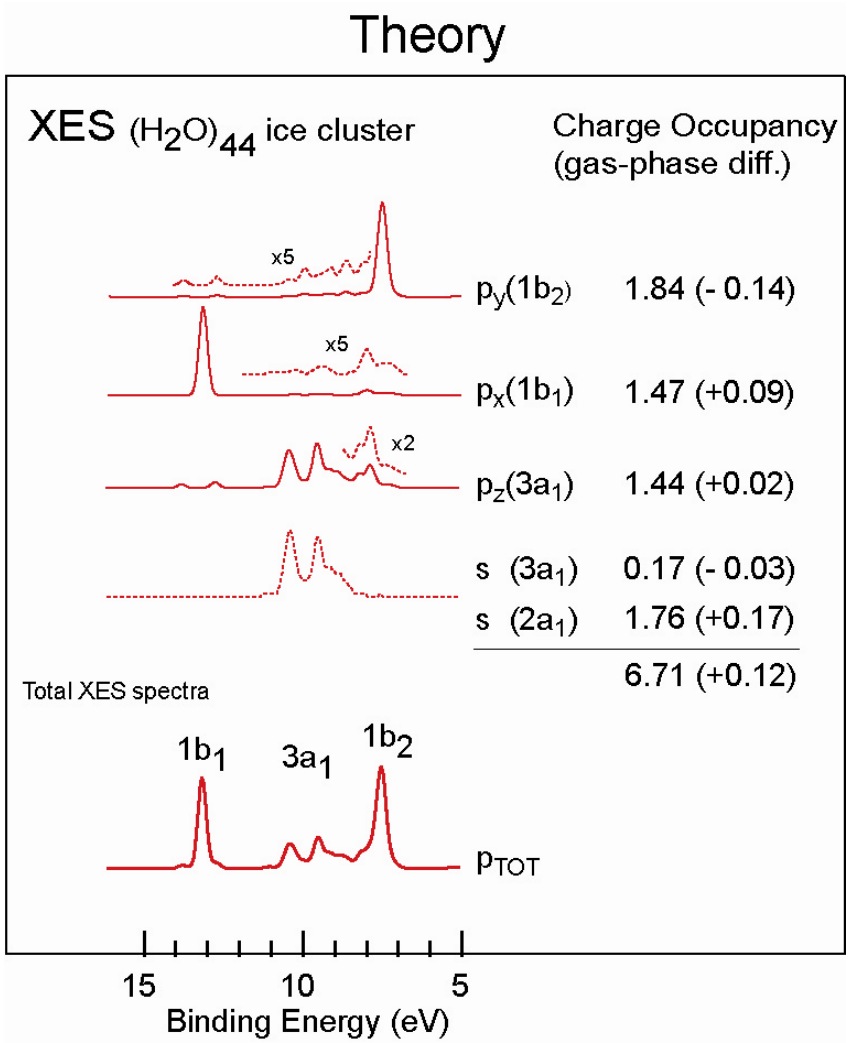


Different dissociation dynamics depends on excitation energy

Odelius et.al. *Phys. Rev. Lett.* **94** (2005) 227401

Occupied orbitals in ice

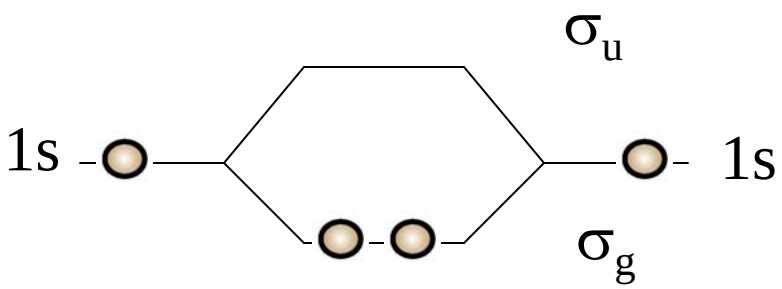


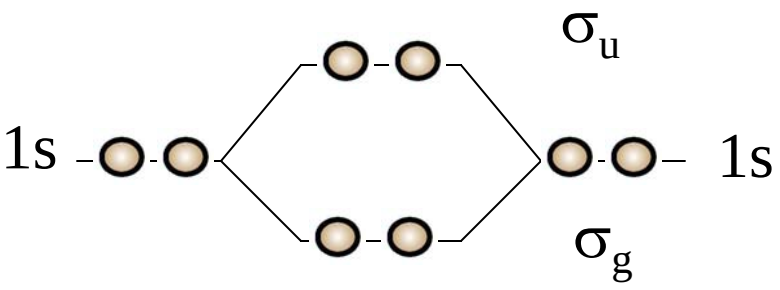


Nilsson et.al. J. Chem. Phys. **122**, 154505 (2005)

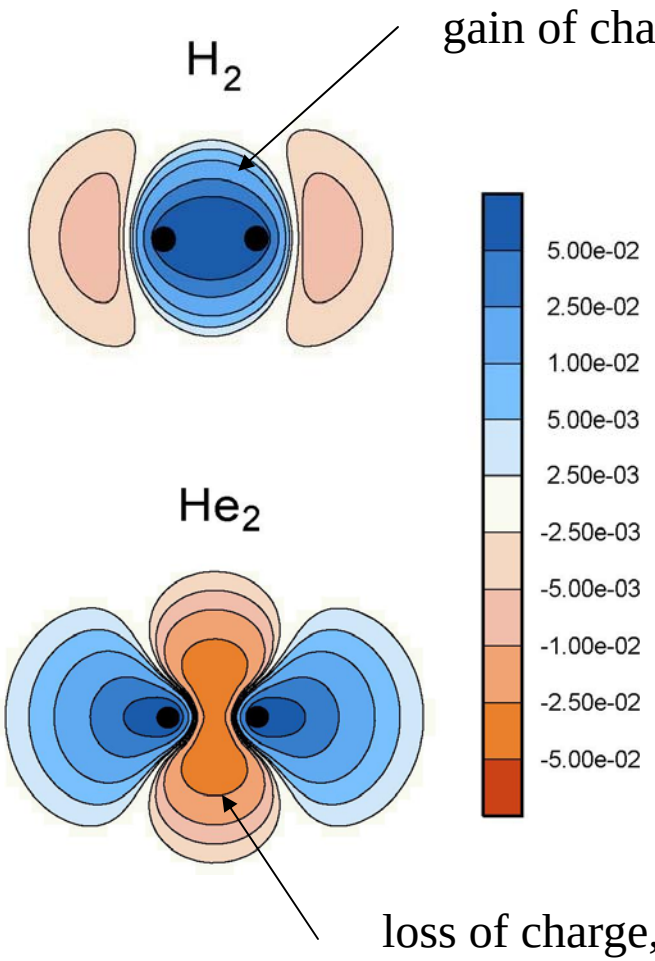
Repulsive and Attractive Covalent Interactions

MO diagram

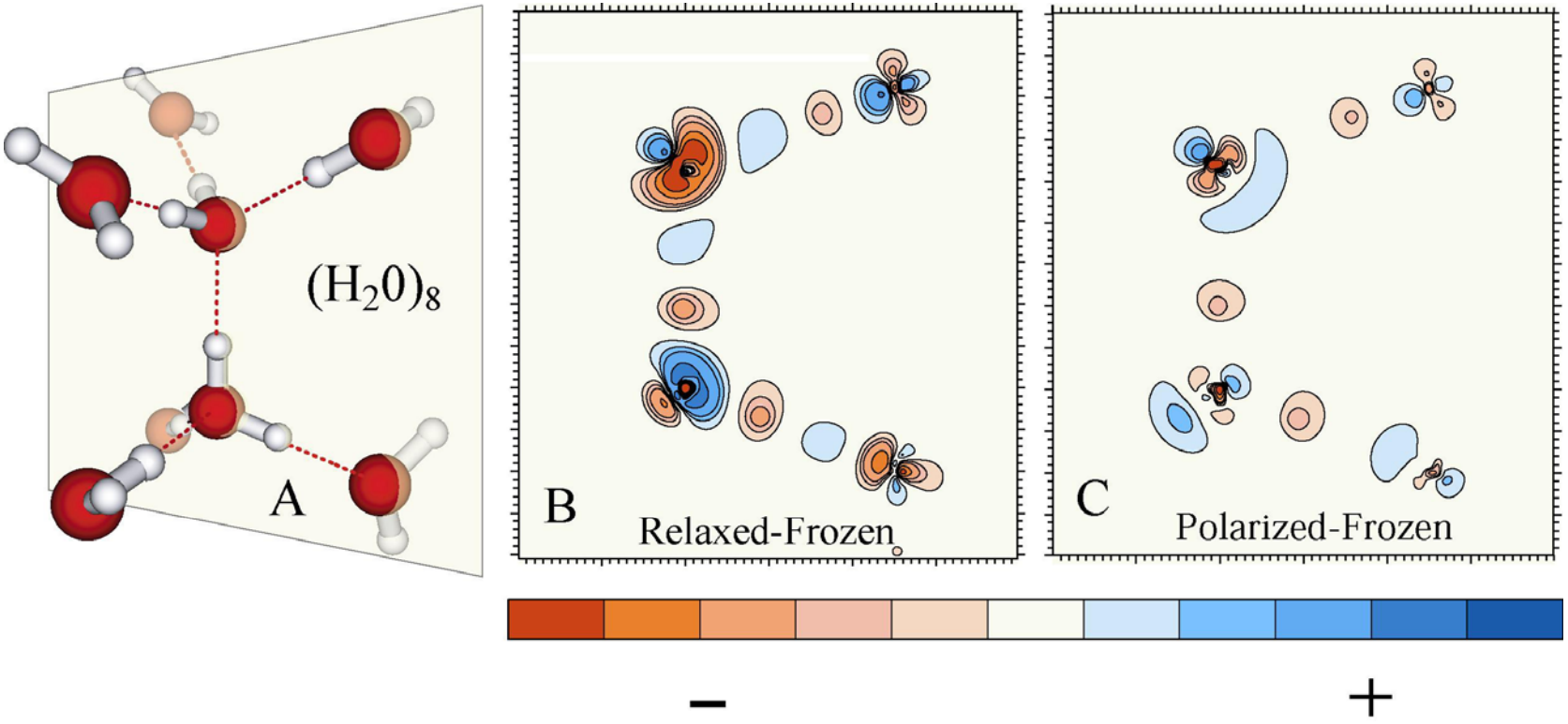




Difference in Charge Density

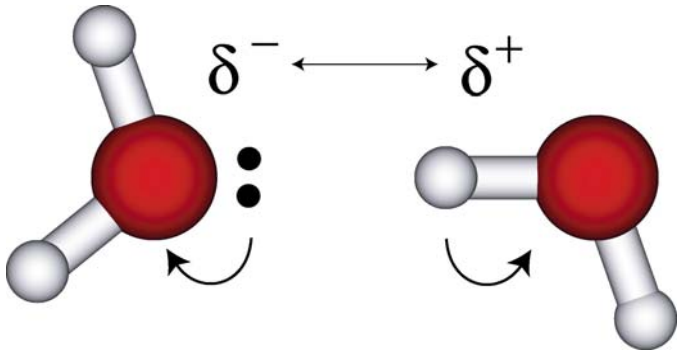


Charge Density Difference plots



Nilsson et.al. J. Chem. Phys. **122**, 154505 (2005)

H-Bonding Principle



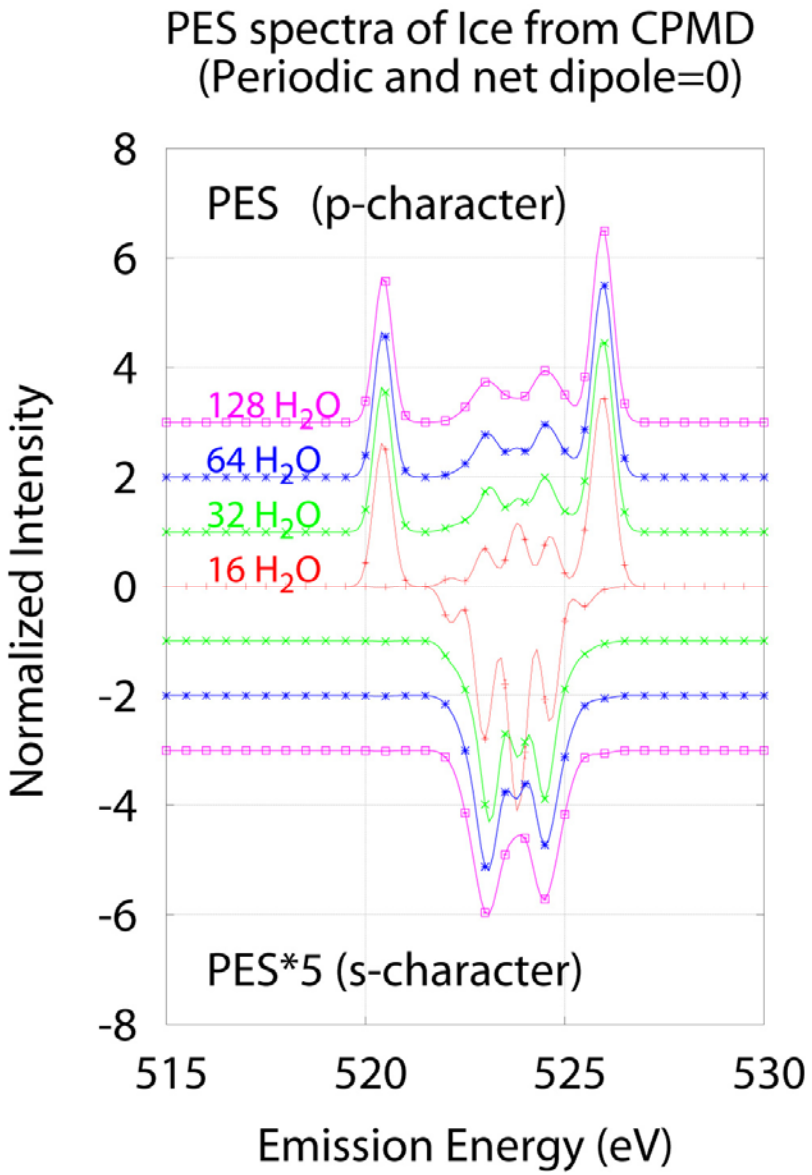
Electrostatic interaction
The units needs to come to short distance

Repulsion Charge transfer between units and s-p rehybridiation to redistribute charge in order to minimize repulsive interaction

How will these effect come in to play in liquid water?

Will the charge transfer effects and rehybridization be smaller for a SD compared to DD species

Long Range Interaction



Strong orbital interaction in the occupied orbitals due to band formation

Large errors with small clusters

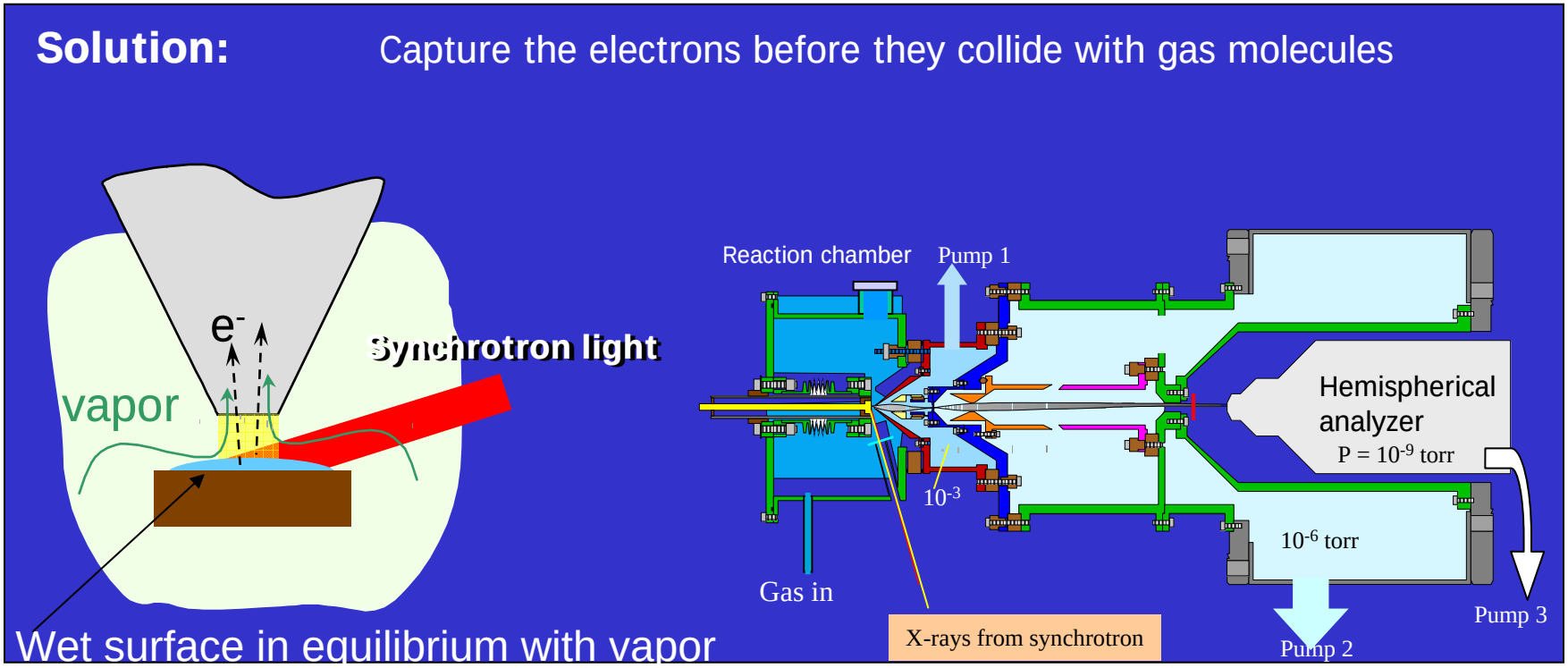
Future direction

Ambient pressure Photoelectron Spectroscopy

Solving the Problem of Scattering of electrons by gas phase molecules

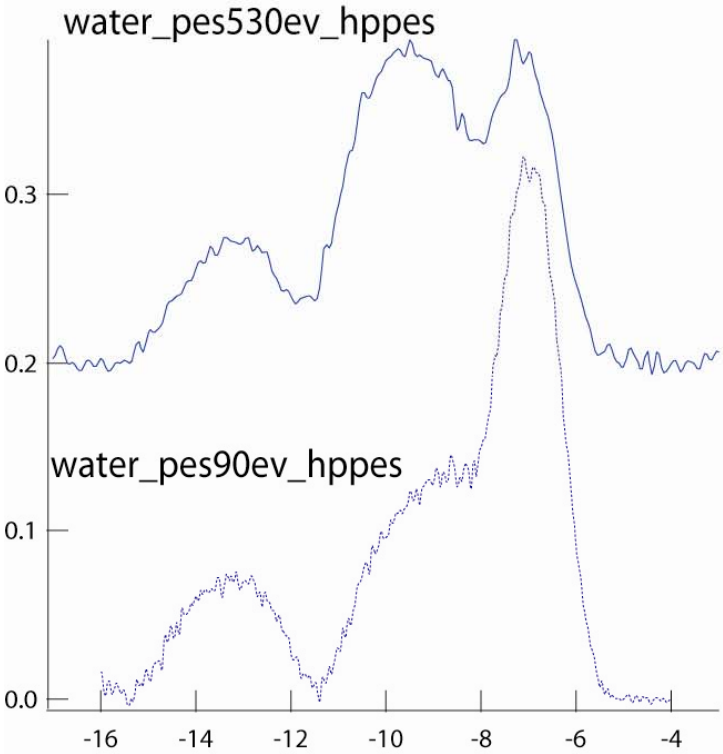
For 500 eV electrons: At P ~ 4 Torr, 1 mm travel. At P ~ 45 Torr, 0.1 mm travel

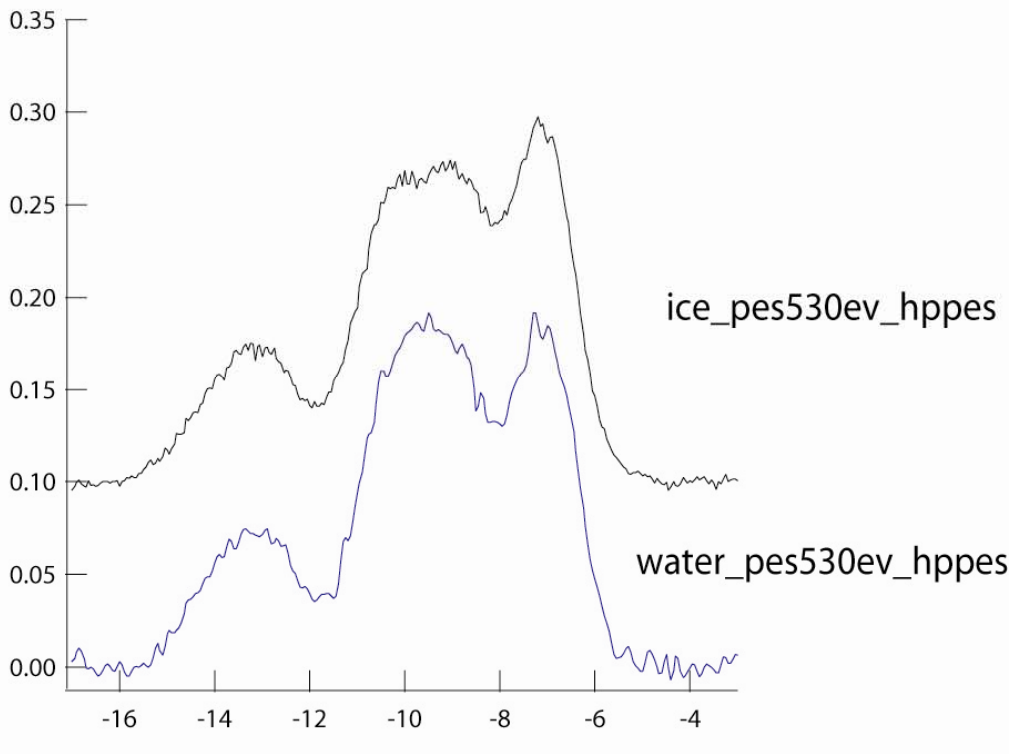
Solution: Capture the electrons before they collide with gas molecules



A differentially pumped electrostatic lens system for photoemission studies in the millibar range
D. Frank Ogletree, H. Bluhm, G. Lebedev, C. Fadley, Z. Hussain and M. Salmeron. **Rev. Sci. Instr.** 73, 3872 (2002)

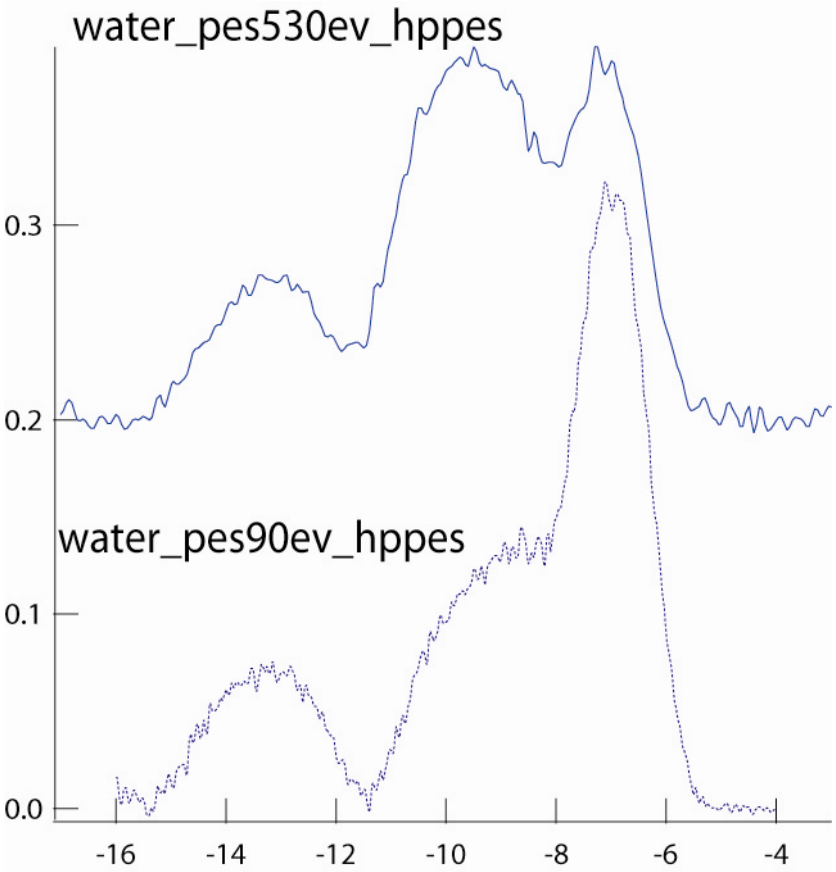
PES on Liquid Water

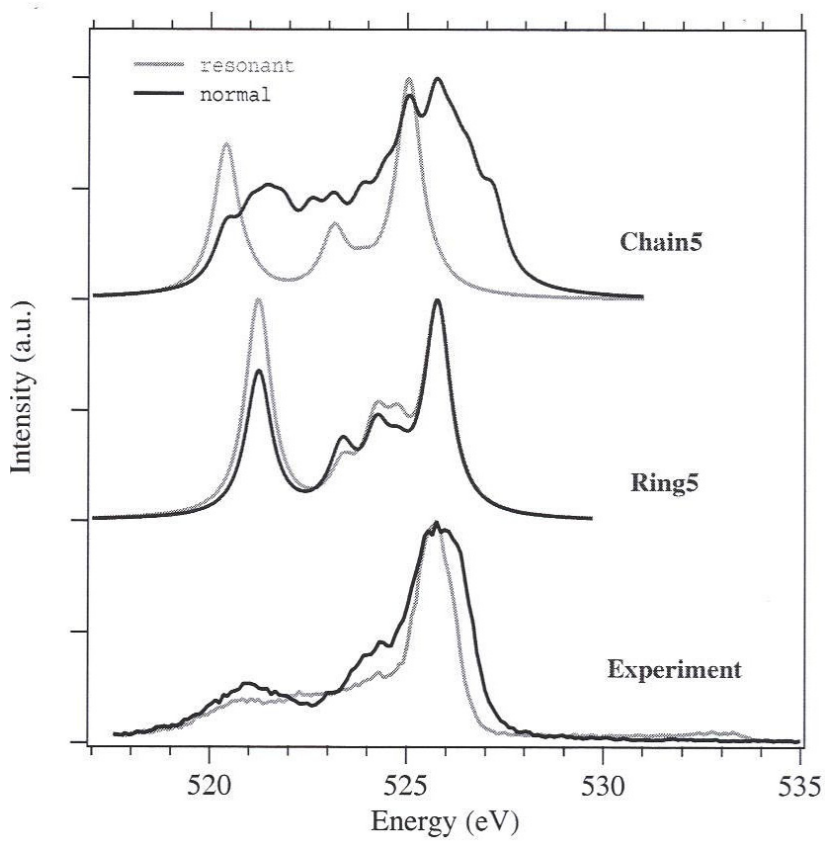




Nordlund et.al. unpublished

Comparing PES and XES



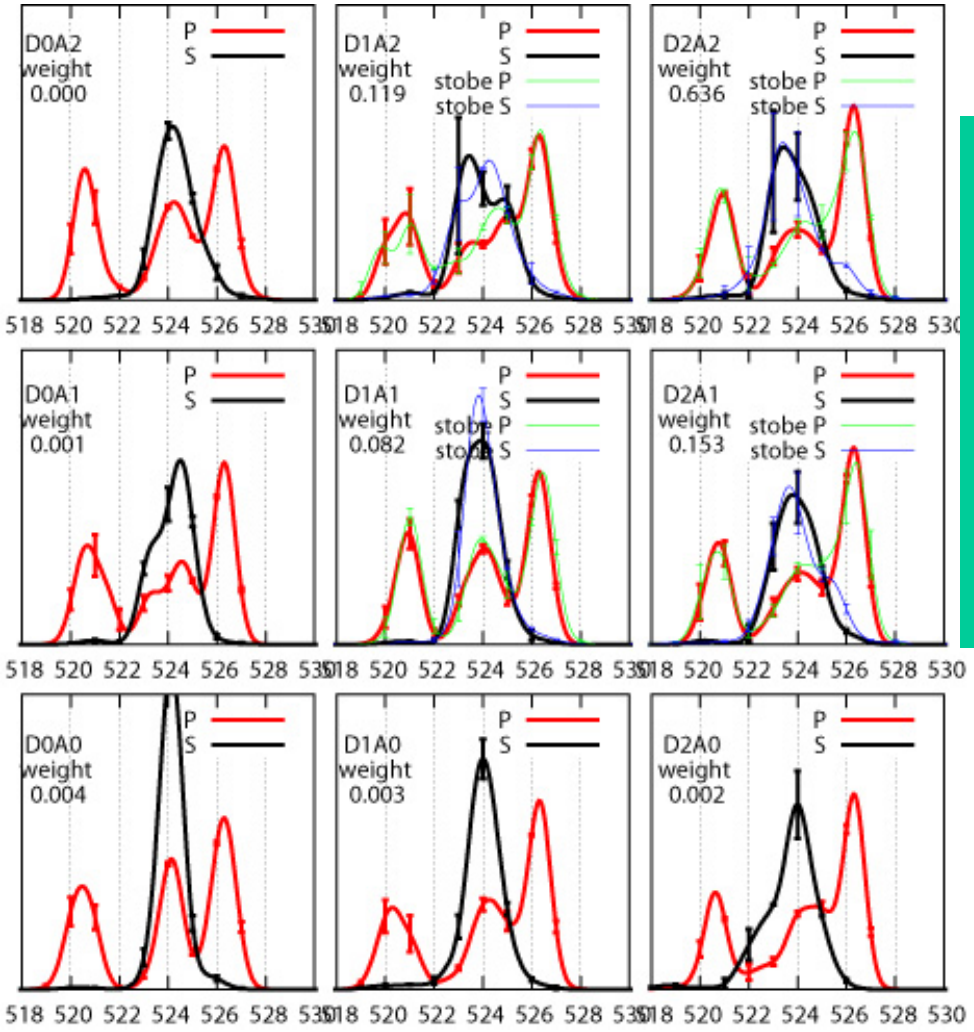


Nordlund et.al. unpublished

Kashtanov PhD thesis , KTH (Stockholm) 2005

Guo et.al. *Phys. Rev. Lett.* **89**, 137402 (2002).

Many configurations



Configurations from CPMD
32 Molecules in the cell
Classifications according to H-bonds

Spectral shape from occupied orbitals not sensitive to H-bonding

Conclusion Controversy

•Half core hole approximation for XAS

Full core hole gives wrong energy scale and no H-bonding resonance in spectra

Half core gives a good agreement with experiment

• Saykally study has severe experimental issues and wrong assumptions for spectral analysis.

Relevance of two component system? Recent PNAS article by the same group

Energetic can be addressed and is consistent with the asymmetrical model

• Liquid water XES spectrum

Smearing of XES spectra due to ultrafast dissociation during core hole lifetime

Theoretical calculations has to include large number of molecules in order to describe the band structure of water

Photoelectron spectra is more a direct measure of the occupied orbital

XAS is more sensitive to water structure than a measure of occupied orbitals